FINAL REPORT

SERDP and ESTCP Expert Panel Workshop on Research and Development Needs for the In Situ Management of Contaminated Sediments

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Table of Contents

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

i

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments
    ii

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

iii

List of Figures

List of Tables

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

iv

LIST OF PRIORITY RESEARCH NEEDS

High Priority Research Needs

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

v

Moderate Priority Research Needs

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

vi

Low Priority Research Needs

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

vii

Characterization of Contaminated Sediments

Sediment Stability

Capping Technologies

In Situ Treatment

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

viii

Acronyms

ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
CERCLA	Comprehensive Environmental Response, Compensation, & Liability Act
COC	contaminant of concern
CSM	conceptual site model
DERP	Defense Environmental Restoration Program
DO	dissolved oxygen
DoD	Department of Defense
DDE	dichlorodiphenyldichloroethylene
DDT	dichlorodiphenyltrichloroethane
EqP	equilibrium partitioning
ESTCP	Environmental Security Technology Certification Program
HOC	halogenated organic compound
K_{oc}	phenanthrene partition coefficient
K_{ow}	octanol-water partition coefficient
MIP	membrane interface probe
MNA	monitored natural attenuation
MNR	monitored natural recovery
MoP	manual of practice
NAPL	non-aqueous phase liquid
NOAA	National Oceanic and Atmospheric Administration
NRC	National Research Council
OSWER	Office of Solid Waste and Emergency Response
PAH	polycyclic aromatic hydrocarbon
PCA	principle components analysis
PCB	polychlorinated biphenyl
PVA	polytopic vector analysis
RCRA	Resource Conservation and Recovery Act
RPM	remedial project manager
SERDP	Strategic Environmental Research and Development Program
SPMD	semi-permeable membrane device

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

ix

TEF   toxicity equivalence factor
TIE   toxicity identification evaluation

U.S. EPA   U.S. Environmental Protection Agency

Acknowledgements

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

xi

1. INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are Department of Defense (DoD) programs designed to support research, development, demonstration, and transition of environmental technologies required by the DoD to perform its mission. Environmental cleanup is one of the major thrust areas. Within this area, contaminated aquatic sediments represent a particularly complex issue that is growing in significance.

1.1 DoD's Contaminated Aquatic Sediments

Aquatic sediments are often the ultimate receptors of contaminants in effluent from DoD activities. Sediment contamination problems are particularly difficult due to the tendency for contaminants to be retained within sediments for a long time. According to an estimate by the U.S. Environmental Protection Agency (U.S. EPA), approximately 10% or 1.2 billion cubic yards of the sediment underlying the country's surface water is sufficiently contaminated with toxic pollutants to pose potential risks to fish and to humans and wildlife that eat fish (U.S. EPA, 1998). This represents the upper 5 centimeters of sediment where many bottom-dwelling organisms live, and where the primary exchange processes between the sediment and overlying surface water occur. Acute laboratory toxicity tests performed by the National Oceanic and Atmospheric Administration (NOAA) on 1,543 surficial sediment samples collected from 1991 through 1997 in 25 estuaries and marine bays representing a total area of approximately 7,300 km^2 indicated toxicity in approximately 6% of the combined area (Long, 2000). Adverse ecological effects from contaminated sediments include fin rot, increased tumor frequency, and reproductive toxicity in fish. In addition, contaminated sediments can also pose a threat to human health when pollutants in sediments accumulate in edible aquatic organisms (U.S. EPA 1998 and references therein).

Sediment contaminants include a wide variety of compounds, including but not limited to, polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), various metals and metalloids, and military-unique compounds such as munitions constituents. These contaminants are the most frequently reported contaminants that dominate the ecological and human health risk associated with contaminated sediments in the country (U.S. EPA, 1998) and in U.S. Navy sites (NFEC, 2002). The sediment contamination problem is exacerbated by the need to periodically dredge the old deposited sediments to maintain navigable depths in waterways. Nearly three hundred million cubic yards of sediment are dredged from U.S. ports, harbors, and waterways each year. It is estimated that approximately 5 to 10% of these dredged materials are impacted with organic and inorganic contaminants.

PAHs are a group of organic pollutants of major concern in contaminated sediments. Many PAHs are on the Agency for Toxic Substances and Disease Registry (ATSDR) and the U.S. EPA's Top 20 Hazardous Substances lists (www.atsdr.cdc.gov). PAHs are also potent mutagens and carcinogens to aquatic and terrestrial animals, including humans (Denissenko et al., 1996; Phillips and Grover, 1994). These contaminants enter the environment predominantly through

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

1

human activities such as the combustion of fossil fuels for transportation and electricity; various industrial processes; biomass burning; waste incineration; and oil, coal, and creosote spills.

PCBs are a mixture of 209 individual chemicals that were used as coolants and lubricants in transformers, capacitors, and other electrical equipment. The manufacture of PCBs was stopped in the United States in 1977 because of evidence that they build up in the environment and can cause harmful health effects. Health effects associated with exposure to PCBs include neurobehavior and immunological changes, and PCBs are also known to cause cancer in animals. PCBs have been found in at least 500 of the 1,598 National Priorities List (Superfund) sites identified by the U.S. EPA (www.atsdr.cdc.gov).

Metals and metalloids including arsenic, cadmium, chromium, copper, and lead are natural earth elements that are released into the environment in excessive amounts due to a variety of human activities. For example, arsenic is used to preserve wood; cadmium is used in batteries, pigments, metal coatings, and plastics; chromium is used for making steel and preserving wood; copper is used in agriculture to treat plant diseases like mildew; and lead is used in the production of batteries and ammunition. Combustion of fossil fuels also releases metals and metalloids in the environment. As with PAHs and PCBs, most metals and metalloids are on the ASTDR and the U.S. EPA's Top 20 Hazardous Substances list.

There is a need for sound science and effective tools to characterize and manage these sites in a manner that reduces risk to human health and the environment and gains regulatory acceptance. As estuarine and coastal sites, in particular, fall under increasing scrutiny, the number of DoD sites requiring action is likely to increase.

The U.S. Navy has formal guidance on addressing contaminated sediments. The Chief of Naval Operations issued its "Navy/Marine Corps Installation Restoration Policy on Sediment Investigations and Response Action" in February 2002. It states that (1) sources shall be identified to determine if the Navy is solely responsible for the contamination; (2) investigations shall primarily be linked to a specific Navy CERCLA/RCRA site; (3) sediment investigations and response actions shall be consistent with Navy policies on risk assessment and background levels; (4) sediment cleanup goals shall be developed based on site-specific information and shall be risk-based; (5) source containment must precede remedial actions; and (6) a long-term monitoring plan with exit strategies shall be developed (Department of the Navy, 2002).

Based on more than 200 identified sites, the estimated cost to complete remediation of the Navy's contaminated aquatic sediments is more than $1 billion. Complexities involved include varying water body types (e.g., marine/estuarine/freshwater) and implications for sediment stability, mixed contaminants (e.g., metals and/or organics), urban environments, resource constraints, consistency in understanding data analyses, acceptance of uncertainty in risk management decisions, local and regional differences in requirements and options, and consideration of current and future use of sediment sites. Within the Navy, larger and more complex sites will likely consider a combination of multiple remedial approaches (i.e., excavation of sources, consideration of in situ treatment, containment, or monitored natural recovery [MNR] and long-term monitoring).

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

2

Within the U.S. Army, no quantitative analysis of the problem associated with contaminated aquatic sediments currently exists. However, as manager of millions of acres of land, the transfer of contamination from land to surface water to sediments has been observed at a number of installations. These installations tend to be located inland; therefore, they are most often relatively small freshwater sites involving sensitive habitats that have the potential to affect estuarine and marine resources. Contaminants at Army sites include explosives (e.g., TNT and its breakdown products, RDX, HMX), metals (e.g., chromium, cadmium, mercury, copper, lead, and zinc), and organics (e.g., PCBs and PAHs).

Qualitatively, the U.S. Air Force's issues associated with contaminated aquatic sediments tend to be more similar to the Army than the Navy.

1.2 Workshop Objectives

SERDP and ESTCP must determine how their limited research and demonstration funds can best be invested to improve DoD's ability to effectively address its cleanup requirements. The objectives of this workshop were to (1) examine the current state of science and engineering associated with the in-place management of contaminated aquatic sediments, (2) identify the gaps in knowledge and technology, and (3) prioritize those gaps where investments in research and development or field demonstrations could have the greatest impact on DoD's aquatic sediments remediation program. This report, which documents the findings and recommendations of the workshop participants, will serve as a strategic plan to guide investments in the area of contaminated aquatic sediments over the next 5 years by the SERDP and ESTCP programs.

2. METHOD

The SERDP/ESTCP Contaminated Sediments Workshop was held August 10 and 11, 2004, in Charlottesville, Virginia. Sixty experts, including researchers and engineers, from within the DoD, other Federal and state agencies, academia, and the private sector accepted the invitation to participate in the workshop. The list of attendees can be found in Appendix A.

A steering committee composed of representatives from the various sectors aided SERDP and ESTCP in defining the scope of the workshop and determining the format. To address the stated objectives, the workshop was focused primarily on issues associated with the in-place management of contaminated aquatic sediments in estuarine and coastal marine environments since they represent the bulk of DoD cleanup liability. Advancing the science and engineering of in-place management of contaminated sediments rather than dredging offers a greater opportunity to impact future cleanup actions. The sites of interest included those being managed (or to be managed) due to the level of contamination under the Defense Environmental Restoration Program (DERP) as opposed to sites dredged for navigational purposes. Further, the emphasis was on persistent contaminants that represent the primary ecological and human health risks (e.g., PAHs, PCBs, and metals). The workshop was not intended to address regulatory or other policy issues nor the broad issues of risk assessment or toxicology.

To communicate the state of the science and engineering associated with key processes and in-place management approaches, six background papers were prepared and distributed in advance of the workshop. Titles and authors are provided below:

- Cohesive Sediment Stability *(Dr. Tom Ravens, Texas A&M University)*

- Fate and Transport of Sediment-Associated Contaminants *(Dr. Rebecca Dickhut, Virginia Institute of Marine Science and Dr. Nicolas Fisher, Stony Brook University)*

- Characterization of Contaminated Sediment Sites: Conceptual Models and Investigative and Analysis Tools *(Dr. Tim Dekker, Limno-Tech, Inc.)*

- Monitored Natural Recovery *(Dr. Victor Magar, Battelle Memorial Institute)*

- In Situ Sediment Treatment: Technologies, Findings, and Research Issues *(Dr. John Wolfe, Limno-Tech, Inc.)*

- In Situ Sediment Remediation Through Capping: Status and Research Needs *(Dr. Danny Reible, Louisiana State University / University of Texas)*

At the workshop, presentations on the content of the background papers and overviews of the Navy's and Army's perspective set the stage for follow-on breakout group discussions by participants (Appendix B: Agenda). Leveraging the background paper topics, participants identified and prioritized gaps in knowledge and technology during the two breakout sessions. Data gaps were prioritized either as high, moderate, or low priority based on their ability to

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

4

produce a near-term impact on the state of the science, applicability to multiple sites, and potential to significantly lower the cost of characterizing and remediating contaminated sediment sites at DoD facilities.

For the key processes session, participants were divided primarily by expertise. During the in-place management session, participants' expertise was blended to address the approaches simultaneously. Breakout sessions were led by a chair and discussions documented by a rapporteur, who was tasked with compiling relevant sections of this summary document. Following each breakout session, the large group reconvened to review and discuss findings.

Breakout Session I: Key Processes
The first set of breakouts addressed process-related topics, including sediment stability, fate and transport of contaminants, and characterization of contaminated sediments. An understanding of these processes is deemed necessary for effective in-place management approaches. A summary of the scope of each breakout session topic is provided below.

> Sediment Stability Issues: As a component of contaminant exposure pathways, the impact of dynamic environments on sediment stability was addressed. Issues to consider included factors controlling sediment stability, applicable methods to analyze sediment stability, and relevant data analysis, modeling, and uncertainty concerns.

> Fate and Transport of Contaminants: Numerous processes (e.g., diffusion, advection, bioturbation, and degradation) affect the fate and transport of contaminants in aquatic environments. Existing tools and their uncertainties were addressed as well as the need for new tools to assess the role of each process at a specific site. These processes strongly influence the design and success of a management approach.

> Characterization of Contaminated Sediments: The chemical, physical, and biological characterization of contaminated sediments is critical for in-place management. Existing methods and their uncertainties were addressed, as well as the need for new tools to monitor sediments before, during, and after treatment. Characterization at various spatial scales was considered.

Breakout Session II: In-Place Management
The second set of breakout sessions integrated the process-related information in discussing in-place management approaches (i.e., capping; in situ treatment using physical, chemical, or biological processes; and monitored natural recovery). Issues to consider included the advantages and limitations of technologies for specific environmental conditions, current stage of technology development, uncertainties and economics associated with scaling the technology, lessons learned from technology implementation, impact and time frames of risk and concentration reduction, performance assessment, and regulatory acceptance for the technology.

3. KEY PROCESSES

3.1 Fate and Transport of Contaminants

3.1.1 State of the Science and Engineering

In aquatic environments, many toxic chemicals, including PCBs, PAHs, metals, and metalloids, bind to fine-grained particles and concentrate in bottom sediments (U.S. EPA, 1998; Olsen et al., 1982). Therefore, the transport and fate of such contaminants in aquatic ecosystems is largely controlled by processes that take place in or near the sediment bed. In recent decades, we have identified important physical, chemical, microbiological, and biological processes that affect the fate, bioavailability, and effects of contaminants within the sediment column. Details of many individual processes are not well known, nor are linkages among processes. These processes are critical to understanding fate and transport of contaminants as well as for understanding exposure pathways. We need a fundamental/mechanistic understanding to be able to explain the processes we measure and mechanisms that control in situ treatment, and to predict long-term performance of an in situ treatment approach. Many processes work together to determine the fate, transport, and effects of contaminants in sediments. Progress on understanding individual processes is important, but we know that understanding how these processes work together is critical to evaluating the outcomes of cleanup activities. New tools are required to help integrate the mix of processes and determine which are most important at a particular site or sites in general.

The following sections discuss the general categories of processes that impact the fate and transport of contaminants in sediments.

3.1.1.1 Bioaccumulation and Bioavailability

Bioaccumulation of contaminants from sediments by aquatic organisms is the most important process governing the ecological and human health risk associated with contaminated sediments. In general, biological effects can occur only after contaminants are accumulated by organisms; contaminants that are not taken into an organism can elicit no biological effect. Thus, it is necessary to determine what fraction of contaminants in sediments can be accumulated by organisms and whether this bioavailable fraction can be readily predicted to accurately assess the biological effects (risks) associated with contaminated sediments. In general, the more lipophilic the organic contaminant, as indicated by its octanol-water partition coefficient (K_{ow}), the higher its bioaccumulation factor (Veith et al., 1979). Also, sediment-water partition coefficients normalized to organic carbon content tend to increase with the K_{ow} of the compounds. Such observations have led to the development of sediment quality guidelines for organic contaminants, such as PAHs, PCBs, and nonionic pesticides, based on equilibrium partitioning (EqP) theory (Di Toro et al., 1991; U.S. EPA 1998). This approach assumes that equilibrium partitioning of organic contaminants between sediments, pore water, and biota is governed by the amount of organic carbon in sediments and the lipid content of resident organisms.

A major problem with this approach is that organic carbon in sediment can be in different forms that may have very different sorption capacities. For example, in addition to natural materials like vegetative debris, decayed remains of plants and animals, and humic matter, sediment organic carbon also comprises particles such as coal, coke, charcoal, and soot that are known to

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

6

have extremely high sorption capacities (Accardi-Dey and Gschwend, 2002; Ghosh et al., 2000; Grathwohl, 1990; Gustafsson et al., 1997; Karapanagioti et al., 2000). Figure 1 shows a comparison of organic carbon normalized phenanthrene partition coefficients (K_{oc}) for different sorbents compiled from several sources (Ghosh et al., 2003). The K_{oc} values for different organic carbon forms span several orders of magnitude. Based on the partition coefficients presented in Figure 1, it is clear that HOCs associated with soot- or coal-type carbon may be orders of magnitude less available in the aqueous phase than HOCs associated with natural organic matter in soils and sediment. McLeod et al. (2004) showed in clam particle feeding studies that the assimilation efficiency for a tetrachloro-PCB was only 1 to 2% via ingestion if the PCB was sorbed to activated carbon, compared to about 90% for PCBs sorbed to diatoms. Current sediment assessment techniques do not account for the nature of sediment organic carbon responsible for contaminant binding. It appears that bioavailability also varies among species and among contaminants in a given condition. Differences in bioavailability could have great impact on decisions about cleanup, but so little is known about the controlling processes that many managers will not even consider it in evaluating cleanup options. Reducing uncertainty about bioavailability could have a great influence on policy decisions.
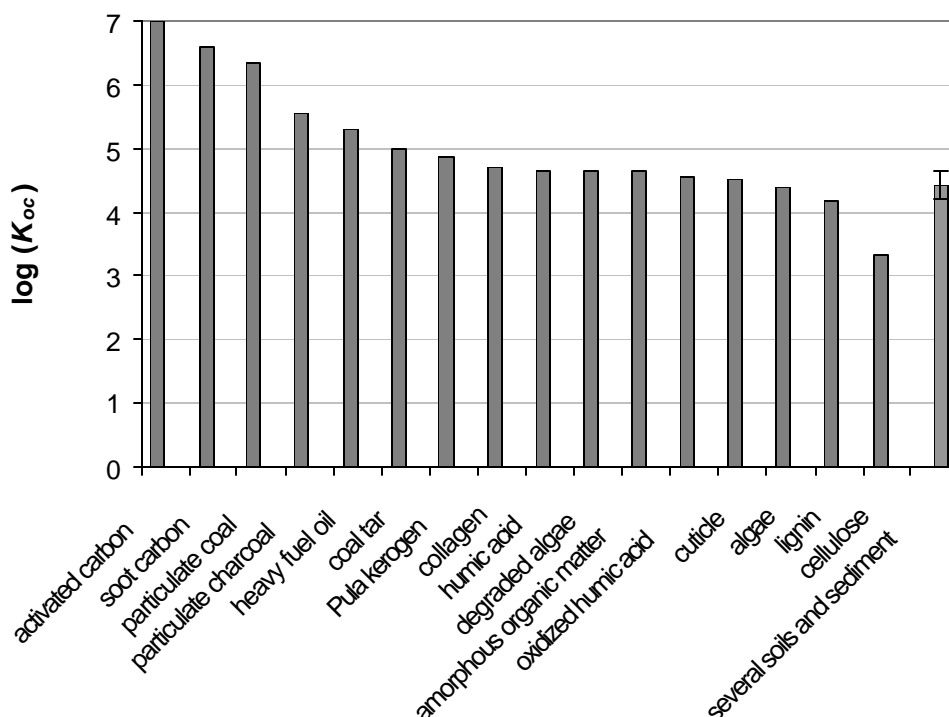
Figure 1. **Organic Carbon Normalized Partition Coefficients for Phenanthrene for Different Types of Organic Carbons (Ghosh et al., 2003)**

For trace metals, large heterogeneities in the distributions of metals in pore waters and the solid phase exist on both temporal and spatial scales that make the use of most models problematic for the accurate determination of metal bioavailability. These heterogeneous distributions of metals can be manifested in tissue concentrations in organisms living in the same patch of sediment. Various studies have shown that within the same habitat or experimental microcosm, metal concentrations in organisms can be highly variable with regard to taxa, mobility, and feeding

behavior (Kaag et al., 1997; Lee et al., 2000a;b; Maloney, 1996). Furthermore, bioaccumulation in general is rarely related to the total concentrations of metals in sediments (Bryan and Langston, 1992; Luoma and Bryan, 1982), nor has it been successful to measure a single chemical fraction that is universally the bioavailable fraction for all metals (Luoma, 1996). These facts have led many to recognize that both the sediment geochemistry and the biology of the specific animal must be understood in order to explain the mechanisms that control metal bioaccumulation.

3.1.1.2 Biodegradation

Microorganisms facilitate the degradation of organic contaminants by acting as catalysts and investing energy to promote biochemical transformations of organic compounds. Aerobic biodegradation of PAHs containing 2 to 5 aromatic rings readily occurs provided the contaminants are bioavailable; however, aerobic biodegradation of PCBs is hindered by Cl substitution on the molecule. In coastal sediments, particularly in estuarine and contaminated harbor sediments, oxygen is rapidly depleted due to the abundance of organic matter that is deposited from both land-derived runoff and autochthonous sources, which leads to high biochemical oxygen demand. Thus, alternative electron acceptors such as iron, manganese, nitrate, and sulfate are utilized in the degradation of organic compounds in all but the very top layer (~0.5 cm) of sediment. Of these, sulfate is the least energetically favored (Libes, 1992), but most abundant electron acceptor derived from sulfate seawater. In general, factors such as sediment aeration and nutrient supply will influence the efficiency of organic contaminant biodegradation. Little is known about the in situ rates of organic contaminant biodegradation in contaminated sediments, and evidence suggests that in situ biodegradation rates in some cases may be much slower than measured in the laboratory. For example, Eganhouse et al. (2000) determined that the in situ rates of reductive dechlorination of dichlorodiphenyldichloroethylene (DDE) (a degradation product of dichlorodiphenyltrichloroethane [DDT]) in sediments off the Palos Verdes Shelf, California were 100 to 1,000 times slower than measured by Quensen et al. (1998) in laboratory microcosms. Currently, the species responsible for biodegradation and the environmental conditions conducive to biodegradation are unknown.

3.1.1.3 Transport Processes

To understand and model the processes controlling contaminant transport from sediments to the water column, and from contaminated areas to lesser or non-polluted sites, it is necessary to quantitatively evaluate particle and associated contaminant resuspension and deposition along with likely mechanisms promoting transport. Wind-wave, tidal, and fluvial forces all generate physical energy in estuarine and coastal areas that can resuspend and redistribute contaminated sediments. In the mesohaline Chesapeake Bay, for example, PAH and PCB fluxes to the water column from current driven sediment resuspension are estimated to exceed settling fluxes by 4 to 20 times, leading to water column residence times of days to weeks (Ko et al., 2003). Such residence times are sufficient to transport contaminated sediments to other regions of the bay. Over time, sediment resuspension and advective transport can act to remove/redistribute a substantial portion of contaminated sediments. The diffusive loss of metals from sediments can be enhanced by alternating redox conditions in sediment and bottom water. In general, metals can be more reactive when associated with Fe-Mn oxides or mineral sulfides, which can be affected by oscillating redox conditions in sediments (Aller, 1994). In addition, the episodic migration of the redoxcline following hypoxic events in enclosed harbors and bays above the sediment-water interface allows the diffusion of metals accumulated in anoxic sediments to

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

8

overlying water. In the absence of significant physical forces, communities of benthic organisms can also facilitate transport of sediment and associated contaminants. Communities of benthic organisms, particularly burrowing organisms and those dominated by head-down deposit feeders, have high rates of sediment bioturbation due to feeding, irrigation, and burrowing activities, and create deep sediment mixed layers (e.g., 25 to 40 cm) (Dellapena et al., 1998). Consequently, burial of contaminants deep within sediments can be significantly slowed by biological and physical processes, and such factors must be considered in selecting a remediation strategy for contaminated sediments.

3.1.2 Primary Data Gaps in Fate and Transport of Contaminants in Sediments

The primary research need in this area is the reduction of uncertainty in risk-based decision making for in situ remediation of contaminated sediments. The research, development, and demonstration efforts should therefore focus on the areas where reduction in uncertainty would make a significant difference in the decision-making process. Three major, overarching areas with respect to the fate and transport of contaminants that need further research are: (1) fate and transport process understanding including in-sediment processes, bioavailability processes, and ecological and human health processes; (2) relationships and interactions among processes; and (3) forecasting, modeling, and integrating tools. A listing is provided below of the high, moderate, and low priority research needs in fate and transport of contaminants in sediments. A more detailed description of the high and moderate priority research needs is provided immediately following this listing.

High Priority Research Needs

A1.   Develop and validate tools and techniques to assess site-specific bioavailability.

A2.   Develop understanding of how sediment geochemical composition influences contaminant partitioning and bioavailability.

A3.   Determine ecosystem shift and species disappearance as a result of the sediment contamination.

A4.   Quantify exchange processes with overlying water and groundwater.

A5.   Develop protocols for building site conceptual models for in situ sediment remediation.

Moderate Priority Research Needs

B1.   Quantify in situ microbial processes of biodegradation and biotransformation.

B2.   Develop methods for simple and inexpensive measurements of the spatial distribution of mixed layer depth in the field.

B3.   Evaluate multiple contaminant interactions on fate and toxicity.

B4.   Evaluate fate and transport processes of sediment amendments.

Low Priority Research Needs

C1.   Evaluate the role of biota in changing contaminant availability, bioaccumulation, and redox (both macrofaunal and microfloral aspects).

C2.   Evaluate the role of contaminants in changing microbial community dynamics and structure in sediments.

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

9

C3.   Develop process-oriented bioaccumulation models that account for biota metabolic processes.

C4.   Develop improved understanding of contaminant transfer through the food chain.

C5.   Evaluate impacts of in situ treatment delivery methods on the ecosystem.

3.1.2.1 High Priority Research Needs

A1. Develop and validate tools and techniques to assess site-specific bioavailability.[1]   Because developing a mechanistic approach to predicting bioavailability has been only partly successful, semi-empirical approaches such as developing relationships between desorption kinetics and bioaccumulation or between surrogates such as SPMDs and bioaccumulation should be investigated as screening tools.   Such bioavailability screening tools need to be validated with biological tests in field conditions.   There are too many models and tools with little validation of biological exposure in the field.   There is need to conduct synoptic chemical, laboratory, and field-scale studies to determine the predictive ability of various chemistry-based tools.   Research should help guide modifications of the tools to enhance predictability.

A2. Develop understanding of how sediment geochemical composition influences contaminant partitioning and bioavailability.   The effect on contaminant partitioning of different carbon types, whether existing in sediments or added as amendments, needs to be better understood.   It is important to understand how sediment composition such as soot, coal, and coke content influence contaminant partitioning and bioavailability of organic contaminants.   Questions remain on the long-term stability of the strongly sorbed fraction of a contaminant.   We need to develop better characterization tools to describe the type of sediment organic matter responsible for contaminant binding.   Research is needed to allow a priori estimation of desorption equilibrium and rates as a function of chemical properties, sorbent properties, and adsorption equilibrium time.   We also need to evaluate if pore water concentration of a contaminant accurately predicts exposure or bioavailability.   Even today, insufficient information exists to assess bioavailability of hydrophobic compounds, redox-sensitive elements like mercury and arsenic, and energetics such as HMX and RDX.   There is a great need for demonstrating to the public and regulators that bioavailability is an important factor in risk assessment.

A3. Determine ecosystem shift and species disappearance as a result of the sediment contamination.[2]   It is well accepted that contaminated sediments ultimately can be connected to threats to ecosystems and contamination of organisms consumed by humans.   The direct connections can be difficult to establish at any site, however.   One reason is that effects of contaminants and/or their trophic transfer to consumable species are not well known.   Another is

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[1] This research need is strongly related to the high priority research needs under Section 3.3 (Characterization of Contaminated Sediments) titled "A8: Develop, evaluate, and validate tools to determine the bioavailability and bioaccumulation of contaminants at sites" and under Section 4.3 (MNR) titled "A31: Develop tools to measure contaminant availability to pore water and ecological and human receptors".

[2] This research need is strongly related to the high priority research needs under Section 3.3 (Characterization of Contaminated Sediments) titled "A7: Develop, evaluate, and validate in situ measurement tools to efficiently monitor the effectiveness of a particular remediation strategy, assess the ecological risk, and assess the ecological recovery at contaminated sites" and under Section 4.3 (MNR) titled "A32: Improve and/or develop ecological screening assays to predict ecological toxicity based on sediment chemistry in assessing the natural recovery of the impacted sediment over time during MNR".

that the precise source of stress that eliminates species is difficult to establish because tools for identifying sources of stress are poorly developed. Ultimately, the ecological effects of contaminants are to eliminate some species from the ecosystem but not others. We know that species' sensitivities to contaminants vary widely, and those sensitivities determine the way communities change in the face of contamination. But, we do not know what causes differences in species' sensitivities and how they relate to contaminant exposure. Reducing uncertainties about what drives different species to be more or less susceptible to sediment contaminants could have great influences on the expectations of what might be achieved by cleanup and the severity of existing effects in environments being prioritized for cleanup. We also need to understand whether species reestablish after remedial efforts and if community structure is comparable to background locale. Some of this work has already been done, but much is needed for sites contaminated with DoD-related chemicals such as explosives, organics, and certain metals.

A4. Quantify exchange processes with overlying water and groundwater. Site characterization at many sites has shown that non-resuspension sediment-water mass transfer can be a very important process for water column exposure and contaminant transport. Current models measure the sediment water flux rate and incorporate it as a lumped, time-dependent, empirically-derived process. Research is needed to understand and quantify the various mechanisms that drive this process, including but not limited to molecular diffusion, groundwater advection, tidal pumping, bioturbation, biodiffusion, gas bubble-facilitated contaminant transport, and direct desorption. Current models use a local equilibrium assumption for computing solid-dissolved phase partitioning in water and sediments. Research is needed to determine when that is a valid assumption for forecasting spatial and temporal trends in exposure. Modeling research is needed to develop models that incorporate sorption kinetics as well as uptake into biota or bioaccumulation into their framework. Bioturbation is important for particle flux and non-particle flux of chemicals such as PCBs from sediments. Advection of groundwater through sediments (i.e., hyporheic flows) can be a dominant mechanism for transporting a contaminant to the overlying surface water and subsequently to the receptor population. Groundwater-surface water interaction has not been adequately researched to provide field-applicable monitoring/quantification techniques. This will be critical for in situ treatments, capping, and monitored natural recovery. Physical stability of sediments can be influenced by benthic invertebrates and plants. For example, some benthic animals form dense colonies that consist of tubes held together with mucous and in this form, which can vary seasonally, the sediments are much more resistant to erosion; rooted aquatic plants such as eel grass send out runners that stabilize sediments. Algal mats can have a similar effect.

A5. Develop protocols for building conceptual site models for in situ sediment remediation. The first step in understanding fate and transport at a contaminated sediment site involves development of a conceptual site model (CSM). This is particularly important for in situ management to evaluate early on if such an approach is feasible for the site. We need to develop protocols to guide the development of a CSM as done for groundwater remediation by the National Research Council (NRC) committee on intrinsic remediation in 2000. The CSM should be specific to the site focusing on the most relevant processes and should not be built as a generic model incorporating all possible processes. The model development method should be iterative building on new information obtained at each stage of the process. Key to the development of a good CSM is the availability of simple tools to quantify the most important processes affecting

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

11

contaminant fate, transport, and exposure at a site. The CSM can serve as a communication tool among stakeholders, a quality assurance tool that insures that important processes are not missed, and a process model tool for beginning the assemblage of quantitative fate and transport models.

3.1.2.2 Moderate Priority Research Needs

B1. Quantify in situ microbial processes of biodegradation and biotransformation. There are many microbial studies and observations that need to be incorporated in a larger integrated understanding of biogeochemical processes. Molecular tools now exist to get a better handle on 'who is doing what' in the environment, but microbiologists need to adapt these tools to address questions on biodegradation and biotransformation. We need to better understand microbial community interactions such that information on microbial community structure can be used to recognize metabolic potential and make a priori predictions on in situ degradation rates. Several biodegradation processes such as PCB breakdown under sulfate-reducing conditions and the rate of biodegradation of hydroxy PCBs need to be better understood.

B2. Develop methods for simple and inexpensive measurements of the spatial distribution of mixed layer depth in the field. The depth of the biologically active zone (from a few cm to 10s of cm) influences mixing, depth of redox zone, conveyance of sediment and pore water-borne contaminants. The rate of natural attenuation of surface sediment concentrations is very sensitive to depth of the upper mixed layer (i.e., controls the contaminant residence time in surface sediments). We need research to develop methods for simple and inexpensive measurements of the spatial distribution of mixed layer depth in the field.

B3. Evaluate multiple contaminant interactions on fate and toxicity. In most contaminated regions, organisms are exposed to numerous contaminants simultaneously. Currently, there are no systematic ways to elucidate whether multiple contaminants will act additively, synergistically, or antagonistically in their toxicity to organisms. Attempts should be made to provide a rational basis for understanding how different types of contaminants would likely interact. There is a pressing need to approach this problem for metals. The U.S. EPA is in the process of preparing a metals risk assessment framework, part of which will consider interactions. A few models are being developed to reflect current views on this subject, and research is needed to further these models. Certain metals are specifically important at DoD sites, including lead, chromium, cadmium, zinc, and arsenic. The presence of a toxic metal (e.g., nickel) may also inhibit other beneficial microbial processes, including biodegradation of contaminants. This needs to be better understood.

B4. Evaluate fate and transport processes of sediment amendments. Several in situ treatment technologies are based on the amendment of sorptive or reactive particles to the sediments. The potential loss of the amendments through resuspension and transport could be a major concern. There is need for improved understanding of the fate and transport processes of amendment materials, especially over the long term.

3.1.3 Summary
By focusing on fundamental/mechanistic processes and on integrating information through robust and realistic models, researchers will be able to reduce uncertainty for risk-based decision making related to in situ remediation of contaminated sediments. The high priority research

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

12

needs therefore are focused on processes where great uncertainties exist such as bioavailability processes, effect of sediment geochemistry on fate and bioavailability, ecosystem effects, exchange processes with water, deployment techniques, and protocols for development of site conceptual models. The improved scientific understanding of the key fate and transport processes of contaminants will enable improved quantification and communication of risk to the public and stake holders. Adequate understanding of these processes is especially important for in situ management of contaminated sediments where contaminants will be left in place but the risk to ecosystem and human health will be reduced through an engineered approach.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

13

3.2 Characterization of Contaminated Sediments

3.2.1 State of the Science and Engineering

3.2.1.1 Introduction and Background

The characterization of any contaminated sediment site is likely to be complex due to the multiplicity of contaminants often found at such sites, the different matrices in which these contaminants are found, the numerous physical compartments typical of such systems, and the highly complex processes governing contaminant exchange between system compartments and subsequent transport and fate. Characterization of such complex systems is challenging and inextricably linked to the development and refinement of a system conceptual model that directs site characterization activities in a meaningful way.

The best approach for contaminated sediment site characterization is from the perspective of conceptual model development and continual refinement. This conceptual modeling approach provides a framework for:

- Developing an initial understanding of a site
- Developing working hypotheses for site behavior
- Directing measurements performed to test hypotheses
- Developing a basis for numerical model development
- Continual model refinement
- Evaluation of the significance of different risk pathways
- Appropriate remedy selection
- Long-term monitoring of remedial action

Site characterization efforts also need to remain firmly rooted in well-defined remedial action goals and objectives. Usually, a site characterization is performed as part of a larger process of remedial investigation, leading to an evaluation of the efficacy of various control measures, which typically have as their goal the reduction of exposure of contaminants to receptors, both human and ecological. Consequently, site characterization needs to start with and remain focused on exposure and risk, and the identification and characterization of the relevant exposure pathways that allow risks to be presented.

The emphasis on risk reduction in goals of site characterization and remedial design has been well-documented in recent academic and U.S. EPA guidance (NRC, 2001; U.S. EPA, 2002a;b). This guidance recommends the development and refinement of a CSM that considers sediment stability and describes an iterative approach that tests and refines hypotheses and re-evaluates site assumptions. It also recommends characterization in the context of risk assessment, evaluating data and model uncertainty, defining remedial goals under a risk-based framework, and tying cleanup levels back to well-defined risk management goals. An effective site characterization, then, is one that identifies present and future exposure pathways, evaluates their significance as routes of exposure, and provides sufficient knowledge of the system to allow design of effective remedial measures. The ultimate goal of site characterization is to provide the information required to make technically informed risk-based remedial decisions.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

14

The conceptual site modeling process starts with an initial CSM that is comprehensive and proceeds through a process of continual model refinement and testing. There are many potential starting points for a contaminated sediment site model. U.S. EPA training materials for conceptual site model development use an approach that focuses on explicit characterization of contaminant sources, pathways, and receptors, following an American Society for Testing and Materials (ASTM) standard for CSM development (ASTM, 2003). Following this guidance, the purpose of a conceptual site model is to:

- Describe a site and its environs
- Present hypotheses about types of contaminants (Sources)
- Present hypotheses about the routes of migration of contaminants, with a focus on the geologic and hydrologic model (Pathways)
- Present hypotheses about receptors and exposure routes (Receptors)
- Test and refine hypotheses through site characterization, and to represent the core of site characterization

An example of a mechanistically oriented CSM framework following this form is shown in Figure 2. It illustrates the numerous processes affecting transport in a relatively complex riverine system and includes relevant transport processes (e.g., advective transport of solids and contaminants, loading of solids and contaminants from tributaries, partitioning of contaminants between dissolved and particle-bound phases, bioaccumulation of contaminants in benthic organisms and algae, and food web bioaccumulation of contaminants in higher trophic level organisms). This model provides a fairly comprehensive list of potentially relevant processes that serves as a starting point for further investigation. Ideally, the list above can be shortened significantly through a process of successive iterations of measurement, testing of hypotheses, and development of a simplified model that identifies and begins to quantify the magnitudes of relevant processes and excludes processes that are not significant. With the proper screening tools, such decisions can often be made early in the conceptual modeling process.

The process of conceptual model refinement and adaptation is highly system-specific. Contaminated sediment sites are subject to many different types and degrees of contamination, are exposed to a broad range of environmental conditions, and can be found in widely varying geologic and geomorphologic environments. Contaminated sediments may be located in rivers, lakes, bays and estuaries, or dam impoundments and may be impacted by tidal or seicheing effects, high flows due to spring runoff, wind-generated waves and currents, or human activities such as dam and lock maintenance, boat traffic, or navigational dredging. Despite the varying complexity of such systems, a few basic rules apply to the development of all CSMs. First, *conceptual models are informed by spatially and temporally appropriate data.* Testing and constraining a conceptual model requires collecting and applying data that is appropriately distributed in both time and space. Contaminated sediment sites often are driven by processes that operate slowly, sometimes episodically and over time frames that may extend across decades. Processes like slow burial of contaminated sediment in a settling basin, progressive dilution of contaminants in riverine sediments due to event-based resuspension, or slow migration of contaminants in a floodplain due to periodic, flood-driven "hopscotching" all take

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

15
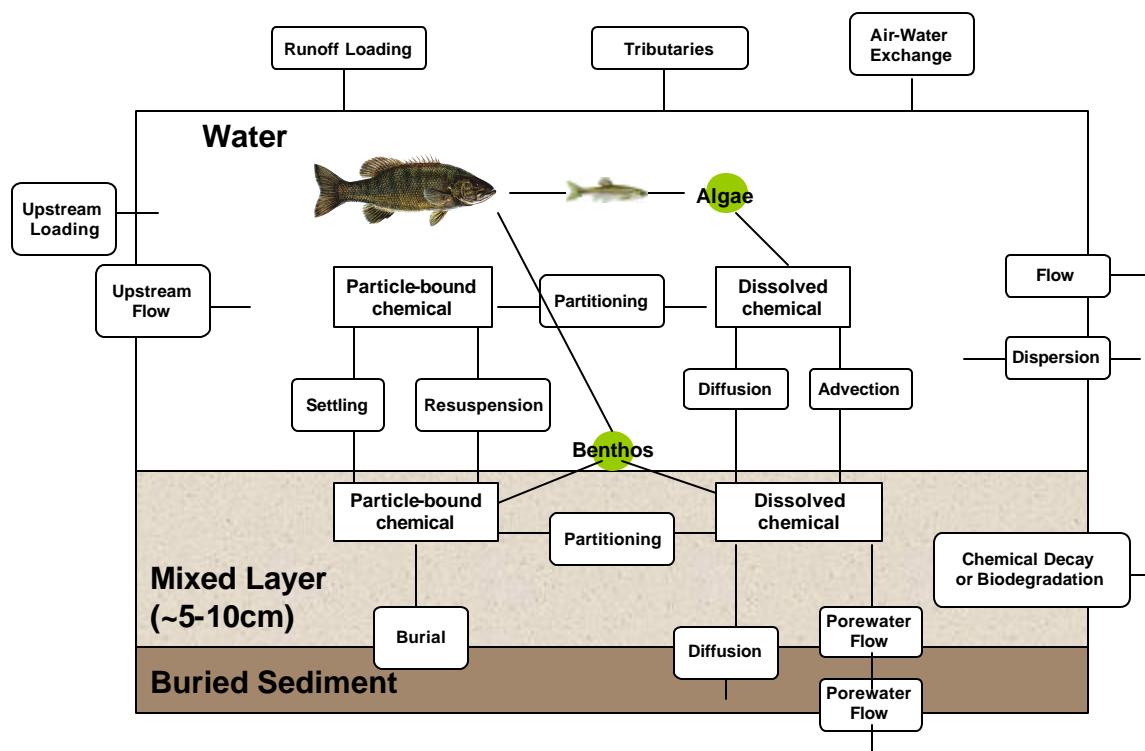
Figure 2. Sample Conceptual Site Model for a River

significant amounts of time and require that measurements be made across appropriately long time scales. Understanding these spatial trends is impossible without data that is well distributed in space. Second, *conceptual models are refined by integrating data from numerous sources*. Testing and constraining a conceptual model is strengthened by integrating datasets that span multiple components of the system under consideration. This general approach is often termed a "weight of evidence" analysis. A well-developed conceptual model, combined with the proper site characterization tools, can provide a means for reconciling different sources of data. A highly constrained conceptual model will provide the linkages necessary to determine the pathways and processes driving the risk at a given site.

3.2.1.2 Tools for Site Characterization

Construction, testing, and refinement of a site conceptual model are usually supported by site investigation activities that require making environmental measurements across all media: water, solids, contaminants, and biota. This section provides an overview of typically applied investigative tools (data gathering) and analysis tools used to organize, interpret, and extrapolate from the available data (data analysis). Often there is considerable overlap between the different categories (e.g., contaminants that are strongly associated with solids conveyed in the water column), but the four categories described here are useful as a rough outline of the sequence by which contaminated sediment sites are commonly characterized: first a water balance, then solids transport, then contaminant fate and transport, and finally food web bioaccumulation. Elements of this typical sequence of investigation are briefly described here. A list of some of the specific tools currently available for making these measurements is provided in Table 1.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

16

Table 1. Available Sediment Characterization Tools

Existing and Desired Tools	Value	State of Maturity (Confidence)	Link to Contaminant F&T and Sediment Stability
Hydrology/Hydraulics/Hydrodynamics			
Flow monitoring-transect velocity, tracer studies, level sensors	High	Field evaluated, high confidence	Required for contaminant/solids mass balance
Ultrasonic flow groundwater seepage meter	High	Field evaluated, moderate to high confidence	Contaminant flux due to advection, sediment cap performance prediction and monitoring. Cannot distinguish spatial and temporal variability well.
Solids			
Water column solids measurements-total solids, dissolved solids, etc.	High	Field evaluated, high confidence	Required for system solids balance. Sometimes used to distinguish between types of solids and establish mechanisms of solids transport.
Side scan sonar	Med/Low	Field evaluated, moderate to low confidence	Bathymetry, potential to monitor sediment deposition and scour
Sediment cores-dozens of coring options available	High/Med	High confidence	Determine sediment properties, grain size, organic carbon, etc. Difficult to assess spatial and temporal variability.
Bank erosion survey-erosion pins or markers	Med/High	Field evaluated, moderate confidence	Bank retreat rate and solids loading to system
Geochronological dating of cores	High/Med	Field validated, high confidence	Measure sediment deposition rates. Evaluate in situ treatment effectiveness.
Dedrogeomorphic measurements and feldspar clay stratigraphic marker	Med/High	Field experience, high confidence	Measures sediment deposition rates.
Contaminants			
Contaminant concentrations in sediment cores	High	Field validated, high confidence	Screen for contaminants, monitor remediation efforts, bioavailability, and exposure. Difficult to capture spatial and temporal variability.
Water column contaminant sampling	Med to high	Field validated	Measure contaminant flux into and out of system. Low contaminant concentrations are a challenge.
Diffusion samplers-e.g. SPMDs, peepers	High	Field evaluated	Measures porewater concentrations in equilibrium with sediment. SPMDs not an equilibrium device. Correlation with bioavailability/flux from sediments not validated.
Diffusion gradient samplers Benthic flux samplers	High	Field tested	Measures contaminant flux at the sediment water interface
Contaminant fingerprinting techniques	High/Med	Lab	Ability to identify contaminant sources. Source affects F&T. Identifying breakdown and weathering products can help monitor remediation effectiveness
Screening level bioassays	High	Lab/Field	Rapid screening of contaminant levels at a site
Sediment Geochemistry			
Natural isotopes (Pb ^{210}, Th, Be)	High	Field validated	Long-term mixing rates of surface/subsurface sediments (=1 yr)
Artificial tracers (pyrite, colored beads)	High	Field validated	Short-term mixing rates (monthly values for annual cycles)
Gypsum plates	High	Field validated	Measures water-side mass transfer coefficients, important for HOC release rates
Trident probe	High	Field evaluated	Sediment temperature, conductivity, redox
Biota			
Rapid bioavailability screening-supercritical CO_2 extraction	High	Lab	Methods to measure the bioavailability of contaminants in a specific sediment
Molecular tools	Med/High	Lab	Rapid screening tools to determine the microbial communities present at sites. Tool to predict biodegradation success at a site
Rapid screening toxicity tests	High	Lab/Field?	Ability to prioritize sites for cleanup, and to monitor remediation effectiveness
Benthic surveys	High	Field validated	Assess importance of bioturbation, cross reference with geochemical mixing to assess the relative importance of physical vs. biological mixing processes to benthic community health.

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

17

3.2.1.2.1 Investigative Tools.

Hydraulics/Hydrodynamics. A critical first step in understanding the dynamics of a contaminated sediment system is to develop a flow balance for the system. Collection of flow data to support such a balance can take many forms, including rainfall and snowfall records, measurement of velocities across a sectioned transect and computing flow, development of stage-discharge relationships from flow and level-sensing data, and measurement of velocities or flows using dye transit and dilution studies. Flow balancing also typically requires consideration of the range of flow conditions, from dry weather, low flow conditions to wet weather conditions that may include over bank flooding.

The connection between groundwater and surface water resources is of increasing interest at contaminated sediment sites. A number of remedial investigations have shown slow leaching of PCB from the sediment bed in the absence of solids resuspension to be a significant vector of transport that follows initial gross transport with the solids. Understanding groundwater and surface water flow or exchange (i.e., hyporheic flows) through the bed in this circumstance is critical. Of particular use is collection of data that vertically profiles temperature or conductivity in the bed (e.g., Trident Probe), hydraulic head (e.g., piezometers across the sediment bed), as well as more direct measures of seepage using drum seepage meters or increasingly sensitive seepage meters that channel flow across a seepage face through a small flow meter.

Water Column Suspended Solids and Sediment Bed Characterization. Following the development of a system flow balance, a common next step is collection of data to support a system-wide balance of solids. This typically includes measurement of water column solids either as total suspended solids or as organic carbon components (total organic carbon, particulate organic carbon, and dissolved organic carbon). It is common also to determine the size fractions of suspended solids. As with flow monitoring, it is critical to gather data under both low-flow conditions and high-flow or flooding conditions in order to capture transport of solids under normal conditions and more turbid conditions under which resuspension of bed sediments may occur. Progressively more refined investigations may be undertaken to discriminate between different types of solids, grain sizes, and mechanisms of solids transport, including event-based resuspension, bedload transport, solids delivery from tributary or overland runoff sources, and biotic solids production.

Sediment bed characterization efforts can help to close a solids balance or test hypotheses suggested by solids data. This is most commonly done using sediment cores, poling studies, and side scan sonar. Collection and visual examination of sediment cores provide hard data on sediment type and can be used to calibrate observations from other techniques. Geochronological investigations of cores can be used to age-date the sediment bed, confirm or refute hypotheses about ongoing depositional processes, and develop estimates of the period of deposition and the susceptibility of sediments to event-based disruption. Poling studies probe sediments with a steel rod and record observations of the depth of probeable sediments, the "feel" of sediments as an indicator of sediment type, and visual observations of the sediment bed. A probing study provides a valuable first indication of the presence or absence of depositional areas, the character and likely erodibility of bed sediments, and the energetics of the system as indicated by bedforms, scour holes, or visually observable bank undercutting and erosion. Poling can be used to map a sediment bed surface as fraction consolidated and unconsolidated sediments. A bathymetric study with side scan sonar also can be undertaken to provide a more

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

18

dense collection of bed elevation data, which, if referenced to a fixed vertical datum, can serve as a reference for future measurements of gross bed elevation changes (i.e., shoaling). These data can be used to explain apparent sinks and sources of solids within the system as indicated by water column solids measurements, leading to a well-constrained model for solids transport.

Sediment Stability. Characterizing sediment stability at a site is important for understanding the potential for contaminant transport from the site. Measurements of sediment stability are typically made in laboratory or field settings using sediment flumes. The consistency of measurements between different sediment stability techniques is not optimal, with different measurement techniques using the same sediment samples often yielding results that are an order of magnitude or more different.

Measurement of River Bank Erosion and Floodplain Deposition. River bank erosion is frequently identified as an ongoing source of solids and associated contamination, particularly in rivers that have become "flashy" due to upstream development and enhanced runoff. In these systems, repeat surveys of bank elevations can provide estimates of bank retreat rate and solids loading to the river. Measuring retreat rates requires a high degree of precision in order to capture relatively small changes in bank profiles with time; consequently, erosion pins or fixed survey markers along the bank profile are sometimes used as control points in bank erosion surveys. As with the sediment bed characterization data, bank erosion estimates can help to explain sources of solids to the river system and can help to constrain models of solids transport.

Contaminant Sampling in Sediments and Soils. Contaminant sampling in sediments and soils is typically conducted with different goals in mind at different stages of a project. Initially, screening sampling is conducted to identify which contaminants may be of concern and which can be ruled out early in the process. Later in the process of remedial investigation, contaminant sampling is conducted to satisfy remedial investigation requirements (monitoring) for characterization of nature and extent, and for determining exposure concentrations for both ecological and human receptors (bioavailability). In all cases, considerations of spatial extent, spatial distribution, and expected temporal change factor into planning for how contaminant sampling is conducted. Core samples are often collected along a regular, coarsely spaced sampling grid to determine the nature and extent of contamination. More intense sampling is often done in areas of elevated contaminant concentration. A series of clusters can provide rich data for geostatistical analysis to capture the spatial and temporal variability at the site. Screening-level analytical methods such as bioassay techniques are likely to become increasingly valuable as part of phased, iterative sampling designs. Feeding these observations into a kreiging analysis produces an estimate of soil concentrations that is well informed by both local-scale and regional-scale information, providing a meaningful map of contamination levels at a site. The elements of a good contaminant sampling design therefore includes a phased, iterative approach; consideration of spatial and temporal elements and geostatistical requirements; and consideration of exposure pathways and key receptors.

Contaminant Sampling in the Water Column. Water column contaminant sampling is conducted to support development of a contaminant mass balance that considers fluxes of contaminant into and out of the system. Contaminants present in the water column in the dissolved, sorbed, or colloidal forms are often determined. This is an important part of estimating temporal changes in

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

19

contaminant concentrations and identifying primary factors controlling transport. While sometimes limited by the very low detection limits often required to detect highly dilute, hydrophobic contaminants, water column sampling investigations can provide insight into processes operative in contaminated sediment systems.

3.2.1.2.2 Analysis Tools.

Many analysis tools are available for organizing, interpreting, and extrapolating the various types of characterization data described above. While a detailed survey of available tools is not possible within the confines of this paper, a few major classes of analyses bear mention and some basic description.

Conceptual Site Models. Models of environmental systems exist in many forms, from empirical statistical models to detailed, highly mechanistic models of hydrodynamics, sediment transport, contaminant fate and transport, and food web bioaccumulation such as the model in Figure 2. One way of classifying modeling approaches into a series of progressively more complex tiers is shown in Figure 3, which shows empirical statistical and trending models as a first tier, models that calculate process coefficients as a second tier, and a third and fourth tier that progress from mass balance modeling to highly detailed, mechanistic models (Dekker et al., 2004). The division of all model applications into a discrete set of tiers is an oversimplification of a highly complex and system-specific continuum of approaches. Most modeling applications, in reality, are hybrids of several different models that may include elements of several different tiers. Even the most complex Tier 4 model may contain critical elements that are essentially Tier 1 statistical models. However, the development of a tiered structure for describing models is valuable as it establishes a vocabulary for discussing and comparing models, helping to increase the transparency of the modeling process.

Time Trending Analyses. Careful analysis of time trending is critical to conceptual model development and refinement and requires attention to detail and adherence to statistical rules for detection of significant trends. Time trend analysis requires thorough review of the data for internal consistency of media and method, objective screening of outliers, and appropriate control for confounding factors such as special trending of organic carbon content in sediments, or species/length/weight/sex in fish or other biota. Trend analysis techniques should also take into account the distribution of the data, the degree of clustering in time, and temporally confounding factors such as seasonality. Numerous parametric and non-parametric methods exist for trend detection, and must be selected based on careful consideration of the factors listed above. Inattention to detail in trend analysis can (and frequently does) lead to identification of trends that are poorly supported or incorrect.

Spatial Trending Analyses. Identification of spatial trends is subject to many of the same considerations that are critical to temporal trending: a need for review of consistency of media and analytical method, screening of outliers, control for confounding factors, and data distribution and clustering. Geostatistical tools such as variography, kreiging, co-kreiging, and conditional simulation (probabilistic kreiging) provide powerful methods to make the most of available data and to direct the development of highly effective sampling designs. Post-processing of interpolated contaminant concentration maps allows for estimation of highly representative exposure concentrations for human and biological receptors.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

20
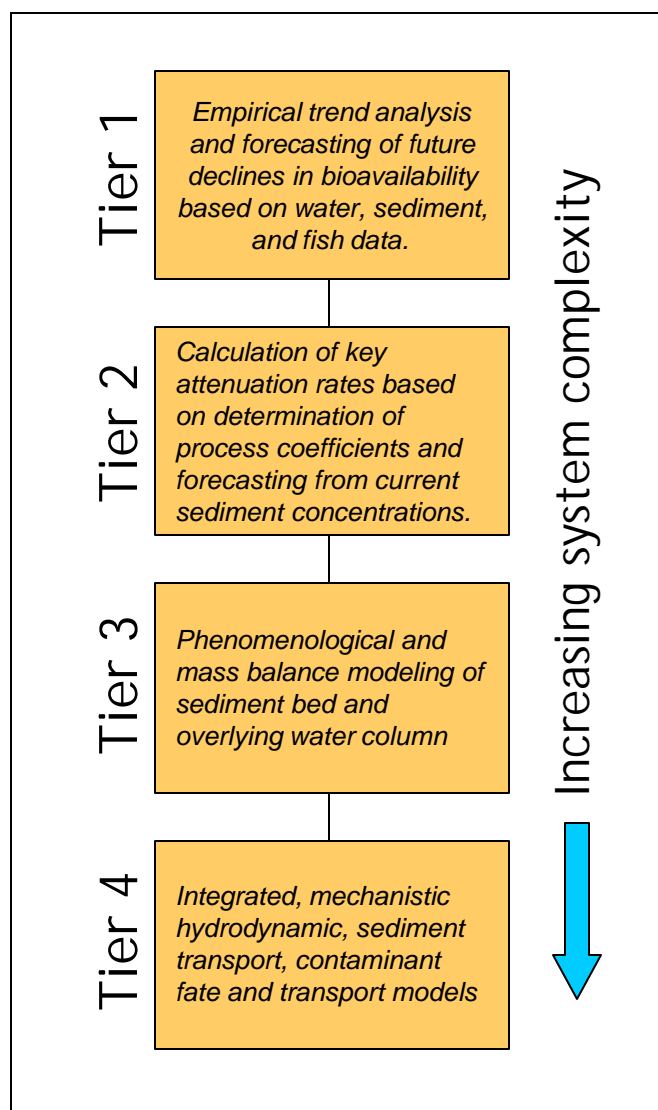
Figure 3. Tiers of Modeling Complexity

Contaminant Fingerprinting and Grouping. Contaminants that are actually suites of different congeners can often be analyzed using techniques that identify covarying patterns in congener distributions, allowing for statistical "unmixing" of different characteristic congener profiles (Barabás et al., 2004a;). These "fingerprinting" techniques (principle components analysis [PCA] and polytopic vector analysis [PVA]) can be of great value in discerning between contaminants with different sources, or in determining the extent to which contaminant congener distributions have been affected by fate processes such as weathering, differential volatilization of different congeners, or dechlorination processes.

3.2.2 Primary Data Gaps in Sediment Characterization

Currently, it is difficult to use first principles to predict the rates of the processes that control the fate and transport of contaminants. Adequate site characterization is difficult and costly due to the lack of tools for this purpose. There is a clear need for rapid, inexpensive, and standardized

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

21

assessment tools to measure the rates and magnitude of the fundamental contaminant fate and transport processes in order to adequately develop and refine a conceptual site model. Additionally, there is a need for improved analysis tools to be able to model these interactions, determine the relationships and interactions among the processes, and to better forecast the success of different remedial alternatives at different sites. A listing of the priority research needs in terms of the tools to collect pertinent process information and the tools to integrate and model these processes is provided below. A more detailed description of the high and moderate priority research needs is provided immediately following this listing.

High Priority Research Needs

Measurement Tools

A6.   Develop, evaluate, and validate site characterization tools to measure the rates of important sediment chemical/physical/biological *processes* affecting the fate and transport of contaminants.

A7.   Develop, evaluate, and validate in situ measurement tools to efficiently *monitor the effectiveness* of a particular remediation strategy, assess the ecological risk, and assess the ecological recovery at contaminated sites.

A8.   Develop, evaluate, and validate the tools to determine bioavailability and bioaccumulation of contaminants at sites.

Analysis Tools

A9.   Improve methods for incorporating uncertainty into measurements of fundamental fate and transport processes and into models for predicting and monitoring remedial alternatives.

A10.   Develop, evaluate, and validate models for predicting success/performance of remedial alternatives to facilitate rapid screening of alternatives at a site.

A11.   Develop, evaluate, and validate advanced tools for chemical fingerprinting of contaminants to identify contaminant sources, improve long-term monitoring efforts, and field validate the kinetics of the fundamental processes measured at a site.

Moderate Priority Research Needs

Measurement Tools

B5.   Develop, evaluate, and validate molecular tools to assess the potential for contaminant attenuation at sites.

Low Priority Research Needs

Measurement Tools

C6.   Develop tools to measure and monitor benthic recolonization rates after capping or dredging.

C7.   Develop tools to screen the potential for beneficial reuse of contaminated sediments dredged from a site.

C8.   Develop methods to predict interactions and contaminant transport between rivers and floodplains.

Analysis Tools

C9.   Develop visualization techniques to better convey spatial and temporal variability

3.2.2.1 High Priority Research Needs

A6. Develop, evaluate, and validate site characterization tools to measure the rates of important sediment chemical/physical/biological processes affecting the fate and transport of contaminants. Most currently available sediment characterization tools are used to bound the extent of a particular contaminant fate process but cannot directly measure the rate of the process. For example, a seepage meter can provide hydrodynamic information but does not directly measure contaminant flux from the sediment. There is a clear need for new in situ sediment characterization tools to provide rate information to a CSM. Basic tools are needed for measurements in the following categories: hydrology/hydraulics/hydrodynamics, solids, contaminants, geochemistry, and biota.

Assuming some conceptual mechanistic model has been developed for a site, non-invasive rapid screening tools that can provide reliable rate measurements for physical, chemical, and biological processes occurring within and between system compartments listed above can be used to prioritize the importance of different fate and transport processes occurring at a site such as contaminant release, or to rule out certain pathways to simplify the CSM. In situ, site-specific geophysical, geochemical, and geobiological identification and measurement tools that result in direct evidence and rate information for each of the processes included in the CSM are needed. Tools can be developed from readily available "off-the-shelf" devices (e.g., cone penetrometers, membrane interface probe [MIP], side scan sonar) available for sediment characterization, or in some cases, a needed tool which does not presently exist must be developed, e.g. rapid bioavailability assays). The following tools are needed for building the elements of the conceptual site model listed:

- *Process identification* - Determine if a specific process is occurring at the site and provide evidence to support it.
- *Process parameter* - Provide the tools to measure this particular parameter at this particular site.
- *Process importance* - Evaluate importance of this process at this particular site.

These tools will provide a better understanding of the fundamental pathways and processes controlling the movement of contaminants from sediments to receptors at each site, and hence a better understanding of the ecological risks. For example, tools are needed to rapidly and accurately assess the redox potential, dissolved oxygen (DO), seepage rates, bed surface area biota (e.g., macrofauna, sub-aquatic vegetation), benthic-layer contaminant flux rates, porewater contaminant concentrations, benthos uptake rates, groundwater-surface water interactions, and erosion rates of cohesive sediments. We are currently unable to predict the rates of contaminant transport processes from first principles, especially at the sediment-water interface, due to the inability to make these fundamental measurements with some degree of certainty.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

23

Identifying tools and methods to couple the biology of an aquatic system with the physical chemical transport of contaminants may provide insight into the processes controlling the fate and transport of sediment contaminants. For example, methods to couple traditional eutrophication models (i.e., N, P, C cycling, algae, zooplankton, fish; bottom and water column) with critical annual cycles (e.g., temperature, light, day-night cycle time) to halogenated organic compound (HOC) chemical fate and transport models could help explain trends that are currently inexplicable (e.g., increased contaminant flux under low flow conditions). Coupling these models could help interpret bioturbation cycles, sediment armoring with algal mats, and sediment protection with subaquatic vegetation. This information is highly valuable for updating and refining the CSM.

***A7. Develop, evaluate, and validate in situ measurement tools to efficiently* monitor the effectiveness** *of a particular remediation strategy, assess the ecological risk, and assess the ecological recovery at contaminated sites.*[3] In situ sediment remediation approaches such as MNR and active capping will require long-term performance monitoring to assess the effectiveness of the remediation strategy, and to monitor the ecological recovery. Methods for rapid, inexpensive surveys of pore water and sediment contaminant concentrations and geochemistry could be used to verify the effectiveness of a particular treatment alternative. Similarly, simple methods for in situ chemical flux measurements from sediments are needed to evaluate the effectiveness of the remedial approach. Rapid and inexpensive long-term monitoring tools are also needed. The type of tools required will depend on the remedial action objectives at a site. For example, if the remedial end point is fish tissue contaminant concentrations, a standardized method to accurately measure them, and to incorporate uncertainty into the measurements is needed. There are currently no standardized methods for monitoring the effectiveness of a remedial alternative.

Rapid and standardized methods to screen for ecological risks for a given contaminated sediment site are not established. Current methods, such as total contaminant concentration, have limitations in accurately predicting sediment toxicity at a site. This is particularly true for sites containing mixtures of contaminants (e.g., PCBs and heavy metals, PCBs and PAHs), which is most often the case. High detection limits, poor reliability, the inability to identify the primary ecological receptors, and the inability to incorporate spatial and temporal variability currently limit their effectiveness. Evaluation tools such as toxicity equivalence factors (TEF) or immunoassays must be developed for sediments containing mixtures of pollutants. A standardized means to apply these tools to chemical mixtures also must be developed. These methods must be demonstrated and validated in the field and ideally would be rapid and inexpensive.

The goal of remediation is often ecological recovery at a site. This recovery can take decades to occur, and it is often difficult to demonstrate that ecological recovery is taking place. Tools are

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[3] This research need is strongly related to the high priority research need under Section 3.1 (Fate and Transport of Contaminants) titled "A3. Determine ecosystem shift and species disappearance as a result of the sediment contamination" and under Section 4.3 (MNR) titled "A32: Improve and/or develop ecological screening assays to predict ecological toxicity based on sediment chemistry in assessing the natural recovery of the impacted sediment over time during MNR.

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

24

needed to monitor ecological recovery at remediated sites. Appropriate indicators must be identified, and methods to measure the rates of recovery are needed.

A8. Develop, evaluate, and validate tools to determine the bioavailability and bioaccumulation of contaminants at sites.[4] The fundamental processes controlling bioavailability and bioaccumulation of contaminants in sediments are poorly understood and limit the utility of CSMs for describing contaminant fate and transport and for predicting the success of a particular remedial alternative at a site. This makes it difficult to choose between different remedial approaches. Surrogates for rapid assessment of bioavailability are still needed. Caged fish or clams are often used to measure the bioavailability of contaminants, but these tests are difficult to conduct, expensive, time consuming, and contain high levels of uncertainty. Semi-permeable membrane devices (SPMD) or XAD resins have been proposed and evaluated as potentially less expensive surrogates to monitor bioavailability of contaminants, but these approaches must be validated in the field.

Bioaccumulation modeling is another area requiring significant improvements. Because the processes responsible for bioaccumulation are not well understood, it is very difficult to predict residual biota levels and to characterize the uncertainty in residual biota data. In particular, it is difficult to distinguish between trophic and non-trophic transfer pathways responsible for bioaccumulation. Without understanding the pathways of bioaccumulation, it is difficult to ensure that remedial alternatives will be effective.

A9. Improve methods for incorporating uncertainty into measurements of fundamental fate and transport processes and into models for predicting and monitoring remedial alternatives. There is a high degree of spatial and temporal variability (heterogeneity) in both the physical and chemical properties at contaminated sediment sites. There is also a high degree of uncertainty in the rates of fate and transport processes at sites, and it is often unclear what site characterization methods are needed to reduce uncertainty in the current CSM. Deterministic models have historically been used to characterize contaminated sediment sites, and these models tend to ignore uncertainty. Standardized methods are needed to incorporate uncertainty into all levels of site characterization, and into all tiers of predictive fate and transport models (based on a CSM). Given the high sensitivity of predictive models to uncertainties, all proposed sediment research should include methods to capture uncertainty in measurements and models.

Several fundamental questions remain regarding uncertainty and methods to incorporate uncertainty into a CSM. For example, it is unclear how much data must be collected to quantify uncertainty at a site. Optimal sampling strategies to capture uncertainty with the minimum number of samples need to be developed, and these strategies should be applicable at different sites. Methods to incorporate spatial variability in transport processes must also be developed. For example, what effect does gas bubble-facilitated contaminant transport have on the total contaminant flux entering the water column if it occurs at some but not all locations at a site, or only at certain times of the year?

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[4]This research need is strongly related to the high priority research needs under Section 3.1 (Fate and Transport of Contaminants) titled "A1. Develop and validate tools and techniques to assess site-specific bioavailability" and under Section 4.3 (MNR) titled "A31: Develop tools to measure contaminant availability to pore water and ecological and human receptors".

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

25

Predicting post remediation residual concentrations at a site is required to evaluate the effectiveness of different remedial alternatives. Methods to better predict residual contaminant levels in biota after treatment and methods to characterize the uncertainty in biota residual contamination data are needed. Ideally, this uncertainty would be included in the remedial action objectives determined for the site. Models including uncertainty must also be field validated.

MNR and in situ treatment technologies such as active capping will require long-term monitoring of performance. Monitoring will take place for decades or longer. There is a high degree of uncertainty regarding the temporal scales to consider when implementing a remedial strategy. For example, how long, and at what frequency should monitoring take place? Riverine and estuarine systems are highly dynamic, and it is unclear what time scales are required between sampling to be able to observe significant changes in contaminant concentrations and/or the useful time scales for updating the CSM. Performance monitoring and CSM updates are time-consuming and expensive so guidance on the frequency that these events should occur could eliminate unneeded sampling and monitoring expenses.

A10. Develop, evaluate, and validate models for predicting success/performance of remedial alternatives to facilitate rapid screening of alternatives at a site. The lack of understanding of the fundamental physical and chemical processes controlling the release and attenuation of contaminants in sediments, and the inability to adequately incorporate spatial and temporal heterogeneity into predictive models, make it difficult to determine a priori the success of a remedial objective at a given site. Given the high cost of deploying the incorrect or inadequate remediation strategy, the ability to predict, with confidence, the success of a given remedial strategy at a site is a high priority. Adequately predicting post-remedy contaminant residuals at a given site (e.g., after dredging or capping) would greatly improve the ability to compare the cost-effectiveness of these approaches. Characterization tools are needed to assess the exposure pathways and the ability of a given remedial alternative to reduce or eliminate those pathways. Data (and uncertainty) from these tools must be incorporated into the CSM, adequately accounting for the spatial heterogeneity at the site. The same tools also can be used to guide post-remedial monitoring and predictions of time to reach remedial action objectives.

A11. Develop, evaluate, and validate advanced tools for chemical fingerprinting of contaminants to identify contaminant sources, improve long-term monitoring efforts, and field validate the kinetics of the fundamental processes measured at a site. It is becoming apparent that the source of contamination can affect its fate and transport, so identifying contaminant sources can help to better refine the CSM. Chemical fingerprinting of contaminants is being evaluated as a tool for identifying contaminant sources. For example, PCB congener compositions at a site have long been compared to signature compositions of Aroclor 1242 or 1260 to determine their sources, but the degree of confidence in these assessments is low. More advanced methods, such as principle component analyses, can be used to distinguish sources with more confidence, but these techniques have not yet been standardized or validated. There is a high potential for these tools to be useful for long-term monitoring of remediation efforts at a site. For example, these techniques could be used to statistically demonstrate that contaminant degradation is occurring by identifying contaminant breakdown products and correlating them

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

26

with the loss of the parent compound. It is important to make these tools more mainstream through better standardization methods and demonstration projects.

3.2.2.2 Moderate Priority Research Needs

B5. Develop, evaluate, and validate molecular tools to assess the potential for contaminant attenuation at sites. Contaminant biodegradation at sediment sites, particularly for capping and MNR sites, is an important process for contaminant mass reduction. Currently, it is difficult to predict the potential for bioremediation at a given site a priori because the fundamental physical and chemical processes affecting bioremediation are unclear. New molecular tools are becoming available to assess the microbial communities present in sediment, and if the microbes responsible for contaminant degradation are known, these could provide the ability to predict the likelihood of contaminant attenuation at a site. This will require tool development, modeling, testing, and validation. These tools could be used for predicting the success of biodegradation at a site, and potentially for monitoring if the presence of particular organisms can be correlated with degradation.

3.2.3 Summary
The ability to adequately characterize an aquatic system will enable development of non-invasive rapid screening tools to help identify and measure the kinetics of the physical, chemical, and biological processes controlling the exposure pathways to receptors. Improved estimates of the rates of mass transport from sediment to receptors, along with improved analysis tools, will refine the conceptual site models. Ultimately these models will be able to predict the success and/or accurately extrapolate outcomes of different remedial actions at a given site. The tools developed will also provide methods for rapid and inexpensive long-term monitoring of remedial actions at a site. This is particularly useful for in situ remediation alternatives (e.g., capping and MNR) where long-term monitoring requirements are expected to be higher and to continue for long times.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

27

3.3 Sediment Stability

3.3.1 State of the Science and Engineering

Understanding sediment stability in the context of contaminated sediment management strategies is a significant environmental challenge. Billions of dollars will be spent in the next decade to remediate contaminated sediments found within our nation's waterways. In large part, remedial strategies, and consequently costs, will be driven by an understanding of sediment bed stability.

We herein consider the concept of sediment stability to include the potential for sediment resuspension, reworking, transport, and deposition by physical or biological processes. These processes result in episodic cycling of contaminants and sediment between the bed and the water column, and can be followed by longer-term burial in areas of net deposition. Resuspension is the process by which the surficial layer of sediment is eroded from bottom sediment due to an increase in hydrodynamic stress and turbulence intensity and/or weakening of sediment resistance. Reworking generally refers to mixing processes that occur within the bed, such as bioturbation, bedform migration, and deformation. Deposition is the gravitational settling of particles from the water column to the bed. Importantly, for cohesive sediments, the physical properties (shear strength, aggregate size, and settling velocity) of sediment that control resuspension, reworking, and deposition potential can change once that sediment is suspended and can also continue to evolve after deposition and burial. The temporal evolution of these properties is generally nonlinear and is influenced by a wide range of physical, biological, and biogeochemical processes that can act within the bed and water column. For non-cohesive sediments (sands and coarse silts), these properties generally do not vary with time.

In aquatic settings with bed slopes less than approximately 0.007, currents in the overlying water column are the primary physical cause of sediment transport. River flow, surface-gravity waves, tides, storm currents, propeller wash, and bow waves are important sources of energy for hydrodynamic sediment transport. On bed slopes greater than approximately 0.007, sediment mass movements driven by gravity can occur. On bed slopes of approximately 0.0005 to 0.007, sediment flows driven by interacting gravity and turbulence in the bottom boundary layer can occur, where sufficient turbulence (supplied by waves and tides) exists to resuspend sediment (Wright et al., 2001).

In addition to physical causes, biological activity (i.e., bioturbation) can rework aquatic sediments. Although both horizontal and vertical particle displacement are produced by bioturbation (Wheatcroft et al., 1989), the primary concern in contaminated sediments is vertical particle mixing (Bentley and Nittrouer, 2003; Wheatcroft, 1990), which can penetrate caps and displace buried contaminated sediments.

Hydrodynamic sediment transport has been studied for centuries, and robust theories that describe flow interaction in bed sediments have existed for many decades. For coarse, non-cohesive sediments (sands and coarser particle sizes approximately 50 microns and greater), robust physics-based theories and models exist that portray observed rates and styles of sediment transport with great fidelity. However, this is not the case for cohesive sediments, such as silts and clays, and sands containing significant concentrations of silt and clay. Numerous models exist that describe the potential for hydrodynamic sediment transport in cohesive sediments. However, most of these models rely on several site-specific empirical constants to define erosion

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

28

rates and shear-stress thresholds. As a result, few such models are considered to be truly "portable." The range of available cohesive sediment transport models and their site specificity has produced a condition wherein there is no "best" answer or model to constrain, describe, or predict cohesive sediment stability. Therefore, with respect to hydrodynamic particle transport, in many cases, we cannot define the accuracy and uncertainty of sediment stability at an acceptable level for decision makers.

The "cohesive sediment transport" problem has been recognized and studied for decades. Ideally, the scientific community would like to provide managers with quantitative models for cohesive sediment transport that can be "carried" from site to site without excessive tuning so managers can quickly and efficiently test scenarios for contaminant remediation. Such models would allow evaluation of multiple proposed solutions over a range of temporal and spatial scales, under environmental perturbations (e.g., floods, storm waves) of variable intensity. Progress has been made, but gaps in our knowledge still exist.

Below, we describe the knowledge gaps that we consider to be particularly important and worthy of funding support. These research topics should be addressed in an integrated fashion and pursued through long-term studies that are closely coordinated. Since a desirable end product is a portable, multidimensional numerical model for cohesive sediment transport that incorporates evaluations of uncertainty and sensitivity, an important first step is to identify the necessary parameters and environmental forces that will drive the model, then begin collecting necessary data and measurements to constrain these model elements. Field study and model verification/validation need to take place over a sufficiently long time frame and in enough different environmental settings to assure (to a reasonable degree) that the model is robust and portable and that its limitations are known.

3.3.2 Primary Data Gaps in Sediment Stability

Presently, it is difficult to define the accuracy and uncertainty of sediment stability at an acceptable level for decision makers. There is a clear need for an integrated research strategy that can reduce the uncertainty and address the data gaps needed for more efficient modeling of sediment stability. The primary data gaps were identified in three general areas: (1) process understanding (e.g., understanding and measurement of individual processes such as sediment erosion or consolidation); (2) relationships and interactions among processes (e.g., the influence of bioturbation on sediment erodibility); and (3), forecasting, modeling, and integrating tools (e.g., development of transient computational models to predict conditions of sediment erosion, transport, and deposition and associated processes). Below, a short discussion of these general issues is followed by a listing of the high, moderate, and low priority research needs. A more detailed description of the high and moderate priority research needs is provided after this listing.

Process Understanding
Multiple bed stability analyses should be conducted where all available data from the site are used, with the goal of standardizing tools and techniques for measuring, quantifying, and predicting sediment stability. Ideally, empirical and modeling studies should be closely integrated. Empirical studies would use site-specific observations to evaluate whether the sediments have been stable through high-energy events that occurred in the past. Examples of empirical analyses using site-specific data include: bathymetric, geochronologic/sedimentary fabric, and geomorphologic evaluations; assessments of temporal and spatial trends in

contaminants of concern (COC) concentrations; and development of sediment and COC mass balances during storms. The level of detail for analysis at a site depends on data availability, acceptable level of accuracy, and resource constraints.

Relationships and Interactions Among Processes
Generally, a single analysis method, using empirical or modeling techniques, will be insufficient for evaluating sediment stability at a site. Uncertainty in the results, due to lack of data or the use of simplifying assumptions, translates into uncertainty about bed stability when only one analysis method is relied upon. For example, our ability to determine cohesive sediment stability at a given location is quite uncertain. Even though a range of the devices are available to test sediment stability and sedimentary process, it is nevertheless difficult to anticipate how much sediment will be eroded due to hydrodynamic forcing of specified intensity and duration. One important reason for this uncertainty is that there has been insufficient comparative analysis of the methods and approaches that are available. A second, less tractable reason, is that cohesive sediment properties and transport processes display non-linear variability in space and time, and are thus difficult to model and predict.

Forecasting, Modeling, and Integrating Tools
Models developed from sediment transport theory and site-specific data provide a means to predict whether sediments will be stable when subjected to an event that has not yet occurred. Modeling studies range in complexity from simple quantitative evaluations of scour depths during a rare storm, to state-of-the-science computer simulations of sediment transport. Development, calibration, and validation of reliable sediment transport models (adapted for contaminant fate and transport study) will produce management tools that can be used to quantitatively predict the impacts of catastrophic events on the sediment bed. The model could predict the location and depth of bed scour due to a flood or storm, sediment advection to and from a site, and associated contaminant burial or dispersal. These results are used to determine changes in surficial COC bed concentrations due to a rare storm and, subsequently, impacts on biota. Together, the results of these empirical and modeling analyses form the basis for a weight-of-evidence approach that is used to test various hypotheses about bed stability at a site. This approach is consistent with the scientific method and can produce a credible evaluation of bed stability. Various studies have demonstrated that a sediment transport model can be an effective tool for evaluating sediment stability.

High Priority Research Needs
A12. Evaluate and validate tools and techniques to reduce uncertainty in specification of critical shear stress, erosion rate, mode of transport, depth of physical reworking, and depositional processes for cohesive sediment.

A13. Develop a standardized approach to propagating uncertainty and representing sensitivity of the processes and interactions controlling sediment stability.

A14. Validate techniques to measure, observe, and predict resuspension events over a range of conditions.

A15. Develop and validate simple diagnostic tools or a classification system that can be utilized for semi-quantitative characterization of sediment stability.

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

30

A16.   Develop and validate models of bottom boundary layer particle-fluid interactions that incorporate complex phenomena observed in field measurements.

Moderate Priority Research Needs

B6.   Validate model predictions of erosion depth, gross and net deposition, and the effects of events on contaminant flux and concentration during extreme events.

B7.   Conduct comparative studies of flume sediment-transport techniques and results to facilitate selection of the correct tools and approach for a particular environmental setting.

B8.   Conduct field-scale studies of sediment dynamics to evaluate new and existing tools, and skill-assess models for sediment transport, ensuring that models incorporate physical, biological, and chemical influences on sediment stability

B9.   Develop computational models (from integrated field trials/model validation described above) to verify the efficacy of the remediation with respect to sediment stability and improve the decision maker's ability to forecast and predict.

B10.   Develop and validate a decision-making framework to help stakeholders select approaches and remedies that take into consideration sediment stability and transport conditions.

Low Priority Research Needs

C10.   Determine the effects of redox oscillating environments on the sediment stability and contaminant dynamics.

C11.   Develop techniques to assess heterogeneity caused by the spatial and temporal changes in the physical properties of the sediment.

C12.   Develop procedural guidance for defining the uncertainty in the bathymetric survey comparison before using these data to evaluate the behavior of the system and model performance.

C13.   Develop a better understanding of how to handle non-uniform flows in sediment transport models.

3.3.2.1 High Priority Research Needs[5]

A12.   Evaluate and validate tools and techniques to reduce uncertainty in specification of critical shear stress, erosion rate, mode of transport, depth of physical reworking, and depositional processes.   A wide range of equations and models have been published that relate sediment physical properties (water content, grain size, mineralogy, etc.) to the resultant sediment transport parameters listed above. Approaches and results for different techniques are broadly similar to one another, but no single approach (or subset of approaches) has been accepted as a standard. In addition, the effects of anthropogenic disturbance (e.g., prop wash) and biogeochemical processes (e.g., bioturbation, biofilms, diagenetic changes in redox

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[5] Two high priority research needs were identified under Monitored Natural Recovery that are related to sediment stability: A26 (Develop, evaluate, and/or validate a characterization tool to assess the stability of impacted sediments) and A30 (Standardize approach on application, interpretation, and use of sediment flume data to assess sediment stability). Readers should refer to these descriptions for additional discussions on sediment stability needs.

chemistry and sediment properties) on the above parameters have not been adequately elucidated and should be closely evaluated. This lack of a standard accepted approach in cohesive sediment dynamics has been a research problem for decades, due largely to the complex and nonlinear behavior of cohesive sediment erosion, transport, deposition, and consolidation. No single short-term research program is likely to solve the problem. However, as a start, existing approaches that specify sediment erosion and deposition parameters should be subjected to close comparative scrutiny with the goal of developing or identifying standard approaches most suitable for particular environmental settings.

A13. Develop a standardized approach to propagating uncertainty and representing sensitivity of the processes and interactions controlling sediment stability. For the purposes of risk assessment, an important component of the sediment dynamics problem identified above is the estimation and propagation of uncertainty for a particular measurement or predicted outcome. Such uncertainty estimates are not widely incorporated into existing research tools, but are necessary for applications in sediment-associated contamination fate and transport.

A14. Validate techniques to measure, observe, and predict resuspension events over a range of conditions. During the past decade, a wide range of new field instruments and technical approaches to study sediment erosion, transport, and deposition have been developed in the marine sedimentology research community, with significant support from the U.S. Navy Office of Naval Research and Naval Research Laboratory. With some exceptions, these new developments have not yet been adopted by researchers in the field of contaminant fate and transport. An excellent summary of some of these topics is presented in Wright et al., 2001, and references therein. Promising new technologies and approaches should be sought out, adapted to, and integrated into studies of contaminated sediment stability.

A15. Develop and validate simple diagnostic tools or a classification system that can be utilized for semi-quantitative characterization of sediment stability. Not all studies of contaminant fate and transport are large enough to involve extensive measurement and modeling. For smaller scale projects or preliminary field assessments, a simplified classification system of potential sediment erosion and deposition rates and thresholds (as well as other parameters) would be useful and cost-efficient. Such tables are commonly used in a range of engineering applications, but a scheme that accurately describes and relates cohesive sediment physical properties to transport characteristics does not exist. This system should be based on field observations and could be an outgrowth of the evaluation/standardization of cohesive sediment transport conditions (and associated uncertainty) described above. Important criteria may include bulk density, mineralogy, water content, organic content, grain size distribution, and salinity.

A16. Develop and validate models of bottom boundary layer particle-fluid interactions that incorporate complex phenomena observed in field measurements. Examples of complex phenomena include near-bed flow stratification, bed reworking, fluid muds, and aggregate behavior. In this area, much can be learned from the marine sediment-transport community, where these problems are presently being addressed (examples in Wright et al., 2001; Bentley et al., 2002; Bentley et al., 2003, and references therein).

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

32

3.3.2.2 Moderate Priority Research Needs

B6. Validate model predictions of erosion depth, gross and net deposition, and the effects of events on contaminant flux and concentration during extreme events. One important consideration for sediment-associated contaminants is the potential for extensive erosion and redistribution of sediment/contaminants during rare and extreme events such as major floods or hurricanes. For such rare events, models and predictive tools for contaminated sediment dynamics are largely unvalidated. However, sediment dynamics during extreme events is an area of active research in the marine geological community (see Wheatcroft, 1990 and Bentley et al., 2002 for examples). Such geological studies have relied on physical and geochronological analyses of cores to constrain factors such as bed thickness and deposition rate, and compared results from cores with numerical model simulations of historical events. Similar demonstration studies could be conducted for specific geological settings to constrain these critical parameters and associated uncertainty, and to provide valuable skill assessment for existing modeling tools.

B7. Conduct comparative studies of flume sediment-transport techniques and results to facilitate selection of the correct tools and approach for a particular environmental setting. Site-specific sediment characteristics that predict sediment erosion potential and rates are commonly evaluated from measurements conducted using in situ or ex situ sediment-erosion flumes. Several accepted designs for erosional flumes exist, and each has been utilized for shear stress and erosion rate assessment in a range of settings. The few comparative studies that have been conducted suggest that results for a specific geological setting may vary depending on the flume design used, but no comprehensive comparison of flume designs has been conducted. Comparison of flume techniques and results would improve predictive capabilities by:

- Determining appropriate range of applicability for each flume
- Determining remediable flaws in each flume
- Developing methods for flume applications
- Comparing flume results to each other and field observations under a range of conditions
- Quantitative measurement of shear stress in each flume

B8. Conduct field-scale studies of sediment dynamics to evaluate new and existing tools, and skill-assess models for sediment transport, ensuring that models incorporate physical, biological, and chemical influences on sediment stability. As new tools and models are developed, they should be evaluated in field-scale studies to skill-assess performance over the widest range of conditions possible. Measurements and model simulations should be closely integrated, not treated as separate entities. Model simulations should seek to predict bed properties based on processes active in the water column, and at the sediment-water interface. Examples of suitable water column measurements include:

- Direct measurements of particle concentration and transport
- In situ measurement of fall velocity
- In situ measurement of turbulent diffusion; and state of the art velocity, particle size distribution, and particle fall velocity sensors to help develop models

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

33

Examples of measured bed properties include:

- Bioturbation and mixing rates from radioisotope geochronology
- Event-related stratigraphy, anthropogenic tracer (Cs-137, metals, etc.) vertical grain-size distributions

B9. Develop computational models (from integrated field trials/model validation described above) to verify the efficacy of the remediation with respect to sediment stability and improve the decision maker's ability to forecast and predict. An important application for sediment-dynamics models developed above (for environmental and economic concerns) would be to allow decision makers to conduct comprehensive simulations of a remediation design performance over a range of environmental conditions and timescales, in order to choose the best remediation approach.

B10. Develop and validate a decision-making framework to help stakeholders select approaches and remedies that take into consideration sediment stability and transport conditions. Many options for assessing and predicting sediment stability currently are available, and no single standard exists. Even if some of the above recommendations are adopted, multiple options will be available for any specific situation. Accordingly, some form of framework should be developed to choose the most suitable measurement and modeling approaches, based on the scale of the project, potential risks, and available resources.

3.3.3 Summary

Predicting sediment stability under uncertain environmental conditions provides a significant environmental challenge for environmental managers. Gaining a better understanding of sediment bed stability will significantly reduce the cost of remediation strategies in the future. This section of the report aims to identify the knowledge gaps that DoD will need to address in order to meet their strategic goals for cleanup and remediation of contaminated sediments in the future. This section of the report defined the following issues as high priority needs for DoD with regard to sediment stability:

- Develop standardized approaches and tools (both instrumental and computational) to specify and estimate critical shear stress, erosion rate, mode of transport, depth of reworking, and depositional processes
- Develop standardized approaches to quantify uncertainty and sensitivity of processes and interactions controlling sediment stability
- Develop and adopt tools, instruments, and techniques to evaluate, measure, and verify actual sediment transport processes such as resuspension events
- Develop a cost-effective and time-effective sediment stability characterization scheme
- Develop and make available models that incorporate complex hydrodynamic phenomena, particle-fluid interactions in the bottom boundary layer, and field validation

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

34

4. IN SITU MANAGEMENT APPROACHES

4.1 Capping Technologies

4.1.1 State of the Science and Engineering

4.1.1.1 Introduction and Background

Most sediment contaminants are strongly sorbed to the solid phase. To a first approximation, containment of the solid phase leads to containment of the contaminants. Thus, significant natural recovery of a body of water can occur simply by deposition of clean sediment over the contaminated layers. Artificial placement of a clean sediment layer by in situ capping can provide significant reductions in exposure and risk by containing the solid phase and by retarding pore water transport processes.

In situ capping can be conducted by placement of almost any type of clean layer, although sand or other coarse media is normally used due to its availability, low cost, and ease of placement. More recently, additives to encourage degradation or sequestration of contaminants have been proposed as cap material. Geomembrane material may be used beneath a cap in soft sediments to aid in the support of the cap and stones, or other large material may be employed as armoring on top of the cap to reduce cap resuspension and erosion. Surficial cap layers may also be designed to improve habitat values of the substrate.

The design objectives of a cap normally include one or more of the following:

- Physical containment of the underlying contaminated sediment
- Separation of the contaminants from biota at the sediment-water interface
- Isolation of the chemical contaminants from the overlying water
- Restoration of suitable ecological habitat of the surficial sediments

Because containment of the solid phase largely contains the strongly sorbed sediment contaminants, one goal of a cap is to ensure that hydraulic forces do not erode and resuspend the underlying contaminated sediment. Since contaminated sediment sites often represent areas of deposition of even fine-grained sediments, sand can often provide adequate stability. When the cap material is insufficient to provide adequate protection, cobble or stone may be added to the top of a cap to provide further armoring against erosion. This may be especially important in near shore areas where wave action or navigational stresses may be significant. Armoring may add considerable thickness to a cap and may also require additional filtering layers to control fine movement through the coarse armor material. Dredging prior to capping may sometimes be proposed to allow cap placement at a depth where it will be subject to reduced hydraulic forces or to avoid significant reductions in water depth.

Separation of the contaminated sediment from benthic organisms that live near the sediment-water interface is one of the most important factors in reducing exposure to and associated risk from those sediments. If adequate separation is provided, direct contact between the sediment contaminants and the organisms can be avoided, reducing the potential for contaminant

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

35

accumulation in the organisms and reducing chemical release due to the physical and chemical changes introduced by those organisms.

Bioturbation, the mixing associated with the normal activities of the benthic organisms, continuously reworks the surficial sediments and the contaminants associated with those sediments. This activity can maintain relatively uniform contaminant profiles in the upper 5 to 10 cm due to effective particle reworking. The presence of a cap of sufficient thickness means that this reworking occurs in the clean cap material rather than in the contaminated sediment. Since the zone subject to the greatest organism activity is typically 5 to 10 cm, even a relatively thin capping layer can effectively eliminate contaminant release and uptake due to bioturbation. The elimination of particle movement by either erosion or bioturbation means that contaminant migration within a stable cap is limited to porewater processes of advection and diffusion. For hydrophobic sediment contaminants, these processes are strongly retarded by sorption onto the immobile solid phase. This elimination of active movement of sediment and the comparatively large contaminant burden the sediment contains is the primary reason that a conventional sand cap is effective.

4.1.1.2 Capping Technologies: Maturity

In general, capping represents a relatively mature in situ management technology (Table 2). Caps made of sand or similar nonreactive materials have been placed over deposits of contaminated materials in waterways for a number of years at the full scale to reduce contaminant flux to the water column and provide clean habitat for benthic organisms. Active or reactive capping, however, is a less mature technology that is considered to hold significant promise for many contaminated sediment sites. Field-scale application of two reactive caps has been deployed only in the last 6 months as part of a demonstration project in the Anacostia River in Washington, D.C.

Table 2. Capping Technology Benchmarking

	Understanding of Underlying Physical /Chemical Processes	**Adequate Laboratory-Scale Research**	**Pilot-Scale Demonstrations**	**Full-Scale Demonstrations**	**Barriers to Technology Use**
Passive Capping	Good	Yes	Adequate	Adequate	Low: risk perception related to leaving contaminants in place
Active Capping	Fair	No	Only one, in early stage of evaluation	None	Significant: lack of basic knowledge, lack of technological options, lack of demonstrations

4.1.2 Primary Data Gaps in Capping Technologies

A number of scientific, technological, and engineering data gaps were identified that, if filled, were considered to have the potential to significantly impact the ability to use active or passive caps for in situ management of contaminated sediment sites within the DoD. A listing is

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

36

provided below of the high, moderate, and low priority research needs in capping technologies for contaminated sediments. A more detailed description of the research needs is provided immediately following this listing.

High Priority Research Needs

A17. Develop and demonstrate active cap amendments for contaminant sequestration and/or degradation.

A18. Assess the ecological impacts of reactive caps.

A19. Develop and demonstrate performance metrics for evaluating capping technology effectiveness.

A20. Assess the efficacy of different cap placement techniques.

Moderate Priority Research Needs

B11. Investigate, characterize, and model the behavior of gases and non-aqueous phase liquids (NAPL) under caps and their influence on contaminant transport through caps, and develop techniques to mitigate these effects.

B12. Investigate and characterize shear forces generated from prop wash and develop a model for the design of caps and cap armoring materials for high hydrodynamic environments such as active port facilities.

B13. Characterize how the biogeochemical environment is altered by placement of a cap and the extent to which these changes affect the fate and transport of contaminants with complex or unknown biogeochemical behavior.

B14. Develop measurement techniques to rapidly characterize subsurface sediments and non-invasive techniques to measure cap integrity.

Low Priority Research Needs

C14. Characterize the effectiveness of thin caps as interim or long-term measures to reduce exposure and bioavailability.

C15. Develop a synthesis of pilot and full-scale capping successes and failures.

4.1.2.1 High Priority Research Needs

A17. Develop and demonstrate active cap amendments for contaminant sequestration and/or degradation. The highest priority research need in capping technologies identified at the workshop was for the development and demonstration of active/reactive cap amendments for contaminant sequestration and/or degradation. Within this relatively broad topic area, there are a number of more specific considerations that need to be addressed. First, amendments must be developed for the range of contaminants of most significant impact to DoD (e.g., PCBs, PAHs, energetic compounds, and metals). While there are many instances where a single type of contaminant dominates the risk and concomitant cleanup criteria at a given site or portion of a site, there are many instances where a range of organic and inorganic contaminants are present, and for this the development of multifunctional caps (i.e., those that address a range of organic and inorganic contaminants simultaneously) is a high priority. Implicit in this consideration is the question of whether contaminants sequestered by reactive cap materials are bioavailable.

This was seen by the workshop participants as a very important question to answer, as it has implications for the long-term risk at the site (e.g., determining the associated risk if a large storm erodes the active cap, which has a high loading of sorbed contaminant, and spreads it around the surficial sediment). Finally, the evaluation of any capping material must also include consideration of the erosion resistance of caps and capping materials, and how the design and optimization of caps will be influenced by reactive material choice.

A18. Assess the ecological impacts of reactive caps. Research is needed focusing on the ecological effects of reactive caps. Aspects include the kinetics of recolonization after cap placement and the ultimate effectiveness of the recolonization (i.e., determining if the cap will support an abundant consortium of organisms at some later point in time). Information is also needed on whether different types of capping materials will affect the structure of the benthic community and whether capping materials (or perhaps sequestered contaminants) will present toxicity to organisms.

A19. Develop and demonstrate performance metrics for evaluating capping technology effectiveness. An important theme that arose in the discussion of capping technologies was a recurrent theme throughout the workshop particularly related to the demonstration and evaluation of technologies: what does one measure to evaluate technology effectiveness? It is critically important to establish a uniform basis for the benchmarking of new and existing technologies. Of course, there will be specific metrics for the performance of caps that will be different from the performance of in situ treatment, for example, but there also should be some uniformity and there are certainly some endpoints that can serve this purpose. Cap uniformity, cap thickness, degree of mixing of the cap with underlying sediment, measurement of porewater concentrations within the upper layers of the cap material, and measurement of seepage flux all may be central to the evaluation of a cap. However, in order to compare the effectiveness of a cap to the effectiveness of in situ treatment, dredging, or MNR, measures must include exposure pathways and exposure endpoints to assess changes in the risk posed by contaminants at a site.

A20. Assess the efficacy of different cap placement techniques. Although in theory a cap may be an effective tool for in situ contaminated sediment management, in practice the cap is only as good as what gets laid down in the field. There are numerous techniques possible for cap placement and a number of different outcomes of cap placement specific to the cap placement method that will influence the final product's integrity and effectiveness. A final research need in the capping technologies area that, again, is ultimately very important in practice, is to assess the efficacy of different cap placement techniques and the additional consequences of each such as differential settling of the cap and underlying sediment, displacement of underlying sediment during capping, and degree of mixing between cap materials and surficial sediment. Each technique will have additional qualities that also influence choice for a given site, including cost, speed of deployment, suitability for finer or coarser grained materials, precision of placement location and uniformity of cap thickness. A thorough understanding of the benefits and disadvantages of different cap placement techniques is important knowledge that would impact the evaluation and practice of in situ capping technologies.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

38

4.1.2.2 Moderate Priority Research Needs

B11.   Investigate, characterize, and model the behavior of gases and NAPLs under caps and their influence on contaminant transport through caps, and develop techniques to mitigate these effects. A second significant gap in knowledge that was identified as having high priority within the capping technologies section was the behavior of gas and NAPL under caps. The first type of data gap identified as being important to fill is the characterization of how contaminants behave under the influence of gas migration under and through caps. To what extent does gas migration mobilize contaminants? Can gas migration and concomitant contaminant transport be modeled effectively, and what are the impacts of gas generation on cap integrity and cap effectiveness? Within the realm of technology development, it is critical to determine how problems associated with gas migration can be mitigated (e.g., by insulating caps to prevent gas generation or constructing treated vents in caps to allow for gas escape). Likewise, NAPL behavior under caps and particularly their behavior during cap placement are not well understood. Research is needed to understand how NAPLs will behave during and after capping takes place, and capping techniques to mitigate NAPL movement and release are important to investigate. Finally, specific amendments, as discussed above, for sequestration of NAPLs and for treatment of gas releases need to be developed and demonstrated.

B12.   Investigate and characterize shear forces generated from prop wash and develop a model for the design of caps and cap armoring materials for high hydrodynamic environments such as active port facilities. The erosion potential of caps was identified above as a priority in the research, selection, and design of a reactive cap. More specifically, very little is known about the shear forces generated from prop wash, which is a critically important issue to resolve for any caps to be placed in active Navy facilities or at facilities that may be slated for use as commercial or recreational harbor. Coupled with this, the design of caps and selection of capping or armoring materials for use in higher hydrodynamic environments is a need for the Navy to enable its use of active or passive capping at numerous sites.[6]

B13.   Characterize how the biogeochemical environment is altered by placement of a cap and the extent to which these changes affect the fate and transport of contaminants with complex biogeochemical behavior. There are many complex physical, chemical, and biological processes that are changed by the placement of a reactive or passive cap. Redox potential, pH, temperature, major ion concentrations, electron acceptor concentrations, and exchange rates with the water column may all be significantly altered. It was considered a medium priority data gap and research need to understand how the biogeochemical environment is altered by cap placement and the extent to which these changes affect the fate and transport of contaminants with complex (or unknown) geochemical behavior (e.g., Hg, As, energetic compounds, and PCBs). The altered biogeochemical environment in which contaminants are contained may have significant impact on the mobility of contaminants through redox-induced speciation changes, may alter the toxicity of contaminants (e.g., methylation reactions), and may influence long-term biologically mediated degradation through mechanisms such as changes in the flux of required

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[6] This ties in closely with the need to accurately estimate shear forces in active areas and the associated sediment resuspension that can lead to cap erosion and a compromise of cap effectiveness (see Section 3.1).

electron acceptors. For some types of contaminants, very little is known concerning their response to changes in the biogeochemical environment (e.g., energetic compounds).

B14. Develop measurement techniques to rapidly characterize subsurface sediments and non-invasive techniques to measure cap integrity. A characterization need that pertains particularly to capping technologies relates to the physical characterization of sediment deposits; this was also identified as a medium-priority research need. Development of subsurface profiling techniques to rapidly measure sediment profiles with respect to shear and compressive strength is important for cap design and placement techniques. Non-invasive measurement of cap integrity with respect to thickness, uniformity, and gas ebullition is an important gap in the current suite of characterization tools that is of significant importance to the short- and long-term monitoring of caps and cap effectiveness.

4.1.2.3 Low Priority Research Needs

C14. Characterize the effectiveness of thin caps as interim or long-term measures to reduce exposure and bioavailability. As discussed in the introduction to this section, the bioturbation layer is typically 5 to 10 cm thick. Placement of a cap of sufficient thickness means that bioturbation would occur in the clean cap material rather than in the contaminated sediment. Since the zone subject to the greatest organism activity is typically 5 to 10 cm, even a relatively thin capping layer may effectively eliminate contaminant release and uptake due to bioturbation. The effectiveness of using thin layer caps as interim or long-term measures to reduce exposure concentrations and bioavailability was identified as an important issue but was relegated to a low priority research need because it may be able to be incorporated into projects addressing one of the higher priority needs.

C15. Develop a synthesis of pilot and full-scale capping successes and failures. Many workshop participants felt strongly that a synthesis of successes and failures of capping experiments (including pilot- and full-scale) was an important research product that would have an impact on in situ sediment management. Such a document was seen as being useful for practitioners and remedial project managers (RPM), but it was also identified as something that could easily fit within other higher priority research projects.

4.1.3 Summary
Conventional in situ capping has proven an effective means of reducing risks associated with contaminated sediments in some situations. There are sites, however, where capping by conventional means may provide insufficient risk reduction or where ambiguities in cap performance goals or implementation feasibility have not provided sufficient confidence in a capping solution. Workshop participants clearly identified the need for fundamental research to develop active capping solutions to improve risk reduction, develop performance assessment measures, and eliminate uncertainty associated with high hydrodynamic environments. Improved characterization of the biogeochemical environment and the physical integrity of an emplaced cap were important research needs. Improving the implementation of in situ capping, perhaps best addressed by field demonstration and pilot-scale work, were viewed as less significant priorities for research, although participants expressed that these were nonetheless important goals that should be addressed within the framework of a larger research project.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

40

4.2 In Situ Treatment

4.2.1 State of the Science and Engineering

4.2.1.1 Introduction and Background

Dredging and disposal of contaminated sediments is the management option employed in the great majority of remedial actions, with capping and natural recovery receiving increasing consideration as in situ remedial options. Although caps may prove durable enough to prevent exposures if properly designed and natural recovery may be sufficiently rapid and irreversible to be protective on some sites, statutory criteria and the precautionary principle have sustained a long-standing preference for dredging in remedial decision-making. Superfund criteria in particular have been difficult tests for in situ remedies to satisfy. In addition to complying with applicable rules and regulations, *Superfund remedial actions must be protective of human health and the environment and meet additional "balancing" criteria for remedial selection, which include long-term effectiveness and permanence; and reduction of toxicity, mobility, or volume through treatment.* A U.S. EPA technical guidance document that is currently in preparation is expected to recommend that in situ remedies be considered for low level wastes, but that close scrutiny be applied to consideration of these remedies in cases presenting high potential risk and uncertainty.

For these reasons, developers of in situ remedial approaches face the burden of demonstrating clear advantages over dredging and disposal in terms of the other Superfund balancing criteria, which are minimizing short-term risks (e.g. due to releases during remediation); implementability; and cost. Nevertheless, the advantage of in situ sediment treatment is that it has the potential for overall protectiveness and permanence, while satisfying the regulatory preference for reduction of toxicity, mobility, or volume through treatment. There is also great potential for reduction in cost, relative to dredging and disposal, by eliminating the need for sediment removal as well as ex situ sediment dewatering, treatment, and solids disposal.

4.2.1.2 In Situ Treatment Technologies: Maturity

With emphasis on in situ amendments to accelerate the destruction or irreversible sequestration of contaminants in sediments, in situ technologies can be broadly described by the reactive catalysts: bioremediation, abiotic remediation, and phytoremediation (Table 3). This information shows that reactive caps and phytoremediation are maturing technologies, having advanced to early field tests. Two of the technologies, sequestration and reactive caps, have as their primary objective reducing exposures by limiting the mobility and bioavailability of contaminants. The other technologies, abiotic degradation, bioremediation, and phytoremediation, aim to reduce or eliminate toxicity by degrading or destroying the contaminant. Each is also potentially applicable as the primary remediation technology or as a polishing step after remedial dredging. Partial treatment leading to risk reduction, such as incomplete degradation of chlorinated organics, may be the best that can be achieved by current technologies.

The technologies also have varying applicability to sites with different characteristics. Abiotic degradation, sequestration, and bioremediation may all be limited in their ability to deliver needed amendments to deeply buried contamination, and active capping does not attempt to treat deep deposits. Phytoremediation is limited only by the depth of penetration of plant roots, but may not be feasible in waters deeper than about 1 meter.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

41

Table 3. In Situ Technology Benchmarking

Technology	Degree of Maturity	Seeks to Reduce	Potential Site Limits	Cost	Other Challenges
Abiotic Degradation	Lab	Toxicity	Depth of delivery	High	Delivery, complete destruction
Sequestration	Lab	Exposure	Depth of delivery	Medium	Delivery, permanence
Reactive Caps	Early field demonstrations	Exposure	Surface fluxes only	Low	Permanence, effectiveness
Bioremediation	Lab	Toxicity	Depth of delivery	Medium	Delivery, complete destruction
Phytoremediation	Early field demonstrations	Toxicity	Floodplains and shallow waters only	Low	Complete destruction

Given the early stage of development of these technologies, their scale-up unit costs can only be estimated very roughly. Each of these technologies has the potential to be cost-effective, relative to dredging and removal. Within this range, we can tentatively assign them to low-, medium-, and high-cost ranges as follows. Abiotic degradation and sequestration are potentially higher cost remedies because they require complete delivery of sediment amendments while minimizing resuspension, and those amendments (including zero-valent iron and activated carbon) have high unit costs. Sequestration relies on natural diagenetic processes which slowly incorporate the contaminant into sediment organic matter; hence, this process is already ongoing and requires acceleration through amendments. The cost may be considered potentially lower than that of abiotic remedies. Bioremediation faces similar delivery challenges but may be able to make use of less costly amendments, such as hydrogen, so it is listed in Table 3 as intermediate in cost. Phytoremediation is potentially less costly and applicable over large areas. This technology derives much of its energy and material inputs from the environment. Active capping potentially saves costs by avoiding any delivery of amendments into the sediment bed.

It is apparent from Table 3 that more bench-scale research and field-scale demonstrations of in situ treatment technologies are needed before they can be routinely applied in the field. What is less apparent but equally important is the need for multiple field tests because of the heterogeneous nature of sediment sites. Although contaminated sediment sites tend to share common attributes, including low-energy hydrodynamics, fine grain sizes, persistent hydrophobic contaminants, and industrial debris and infrastructure, there is considerable site-to-site variability in each of these factors. This makes site-specific remedial approaches necessary for effective management. For example, a technology may prove its effectiveness and permanence in a low-energy site, a freshwater site, or a site that is low in organic matter or debris, but demonstration of applicability to the wider range of conditions requires additional testing on multiple sites having a full range of relevant characteristics.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

42

Based on this assessment, the main challenges for these technologies can be described at a process and technological level, and deal primarily with the physical and chemical challenges that must be overcome to treat sediment contaminants in situ. It should be noted that neither the challenges, nor the research needs will address issues specific to each in situ technology, but rather will focus on broader overarching problems and research opportunities.

The following *process-level challenges* impact cohesive sediments that characterize typical contaminated sites:

- *Adsorption and sequestration* - To treat sediment chemicals, any tendency to adsorb to the sediment matrix must be overcome so extraction and treatment can be applied in the aqueous phase. In most cases, the chemicals adsorb to suspended particles, which then settle and deposit to become associated with the sediment bed. Since sediment organic content is often in the 1 to 40% range, the overall sorptive capacity of sediment particulates can be considerable.
- *Permeability* - The silts and clays that render sediments cohesive result in a very low permeability matrix and make it very difficult to introduce amendments such as solid, aqueous, and gaseous nutrients for in situ treatment.
- *Sediment transport* - Overlying surface waters impact the transport of sediment particulates as a function of a range of physical forcings, including ship wakes, storms, and intentional in situ amendment strategies. This renders sediment contamination very widespread, and the vast scale of sediment sites makes the unit cost of treatment a critical issue.

In addition to scientific challenges, the following *technological challenges* are unique to sediments:

- The apparent need to thoroughly mix amendments into the sediment bed while it is in contact with the water column promotes resuspension and release of contaminants to the water column.
- Operational difficulties of deploying heavy equipment exist on soft sediment beds, whether underwater or aboveground.
- Where residual contaminated materials are left in place, as in active capping, there is the challenge of ensuring long-term stability and permanence of the remedy, and the compatibility of the capping material and embedded treatment additives with the benthic ecosystem that will ultimately colonize it.

4.2.2 Primary Data Gaps in In Situ Treatment

Because of the challenges of delivery, the potential for resuspension, and the strong adsorption and environmental persistence of contaminants, a recent NRC panel (2001) concluded that "in situ treatment and stabilization technologies are unlikely to be used except when the contaminated sediment can be isolated from the water body, for example, through sheet piling or temporary dams". Ultimately, the competitiveness of the in situ technologies will depend on the ability of technology developers to overcome these challenges, in addition to demonstrating effectiveness, feasibility, and cost competitiveness. The types of research needs and the assigned

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

43

level of priority, in addition to those criteria used by all breakout groups, were based on the frequency of occurrence of the need in each of the breakout sessions, and whether the need was identified by multiple stakeholders (academic, consultants, or regulatory) in the workshop. A listing is provided below of the high, moderate, and low priority research needs for in situ treatment of contaminated sediments. A more detailed description of the high and moderate priority research needs is provided immediately following this listing.

High Priority Research Needs

A21. Develop and demonstrate engineering platforms for amendment delivery and treatment.

A22. Perform parallel field demonstrations of multiple in situ treatment technologies to provide performance comparison.

A23. Refine and demonstrate tools and metrics to evaluate pre- and post-remedial impact of in situ treatment.

A24. Develop and assess innovative in situ amendments under a range of sediment conditions.

A25. Develop and/or modify equipment for implementation of in situ treatment that minimizes contaminant release during deployment.

Moderate Priority Research Needs

B15. Investigate technologies that examine the feasibility of in situ treatment, phytoremediation, and bioremediation.

B16. Evaluate contaminant bioavailability and its relation to trophic and non-trophic transfer.

B17. Assess synergistic technology opportunities in addition to individual technology improvements.

Low Priority Research Needs

C16. Investigate technologies for RDX, HMX, and other energetic compounds in light of bioavailability, biodegradation, sorption, and transport.

C17. Investigate the impact of microbial community interactions and dynamics on community function and contaminant degradation.

C18. Develop a fundamental understanding of degradation pathways in support of biodegradation and phytoremediation technologies.

4.2.2.1 High Priority Research Needs

A21. Develop and demonstrate engineering platforms for amendment delivery and treatment. One of the greatest challenges to in situ technology deployment is the need for effective amendment delivery to cohesive sediment matrices. This research need addresses the development and demonstration of fixed and mobile technologies for delivery of aqueous, particulate, and gaseous amendments to treat sediments with minimal sediment resuspension and disturbance of benthic ecologies. The need further emphasizes the requirement that the technology be demonstrated at an 'appropriate scale,' allowing for properly constrained cost and feasibility evaluation.

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

44

A22.   Perform parallel field demonstrations of multiple in situ treatment technologies to provide performance comparison. Site specificity of sediment matrices, physical forcings, and contaminant history hampers effective technology transfer between sites. This research need calls for deployment and demonstration of multiple technologies at multiple sites with widely differing characteristics to develop performance metrics (e.g., short- and long-term effects of technology on sediment stability, contaminant flux, and ecological communities).

A23.   Refine and demonstrate tools and metrics to evaluate pre- and post-remedial impacts of in situ treatment. This need calls for research in the development of non-invasive (remote) technologies for characterization of sediment stability, contaminant fluxes (porewater, particulate, and gaseous) from sediment, and treatment effectiveness. Standardized methods to assess treatment effectiveness should be designed to allow for performance evaluation of individual treatment technologies and be applicable to comparison of multiple technologies. Specific examples of projects include:

- Subsurface profiling techniques to non-invasively measure cap integrity with high resolution (e.g., gas ebullition and thickness)
- Review, develop, and verify a suite of tools and methods for monitoring ecological system improvements, variability, and (where applicable) limitations
- Development of meaningful cross-technology performance metrics (risk endpoints, surrogate measures, long-term effects and monitoring, potential for recontamination)
- Development of cost-effective, easy-to-implement measurement techniques (suite of tools) to quantify aspects (boxes and arrows) of the CSM
- Risk assessment methods for the technologies applicable over the life cycle of the remediation process

A24.   Develop and assess innovative in situ amendments under a range of sediment conditions. This research need emphasizes the requirement for an understanding of the scientific basis for novel amendments and the associated performance metrics under a range of sediment conditions. The emphasis of this research need includes amendments for microbial degradation rate enhancement, contaminant flux mitigation, minimization of byproduct formation and degradation bottlenecks, novel materials/coatings for abiotic particles, demonstration of contaminant destruction and sediment stabilization in phytoremediation technologies, and multivariate sediment-performance models. The emphasis of the technology development and performance assessment should be at the mesoscale. These elements should be applied to the following areas recognized to have the greatest impact on the potential for implementation:

- Bench-scale research and demonstrations of active cap amendments (i.e., lifetime, toxicity, design, and erosion resistance)
- Development of amendments and combinations of amendments for degradation/sequestration

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

45

A25. Develop and/or modify equipment for implementation of in situ treatment that minimizes contaminant release during deployment. Novel in situ treatment technologies need appropriate large-scale equipment for scale-up to the field. Often the success of a novel remediation technology developed in the laboratory will depend on the technical and financial feasibility of scale-up. We need to identify mechanical systems that are used for other similar applications or that can be modified to achieve deployment of in situ treatments in a way that minimizes contaminant release and transport. New tools are needed for efficient deployment minimizing adverse effects to ecosystems. We also need to address how deployment systems will change fate and transport processes and exposure mechanisms.

4.2.2.2 Moderate Priority Research Needs

B15. Investigate technologies to examine the feasibility of in situ treatment, phytoremediation, and bioremediation. There is a great need to identify appropriate sediment and technology characteristics that allow decisions for specific technologies' feasibility to be made. This need focuses on issues such as genetic tool development and application for functional and ecological screening of microbiota, tools for short-term ecological effects (e.g., DNA adducts), and empirical relationships linking multiple endpoints with multivariate sediment characteristics. Specific projects include:

- Develop more accurate (better constrained) and precise models for remedial decision making and assessment
- Apply molecular tools in the field to improve understanding of microbiology
- Develop tools to use in evaluating and selecting remedial technologies (e.g., decision trees, cost estimation)
- Develop a systematic integrated approach for comparative analysis of alternatives
- Develop methods to quantify the impact of contaminant bioavailability on bioremediation success/techniques aimed at enhancing contaminant bioavailability
- Assess short- and long-term limitations of bioremediation as the result of contaminant bioavailability to microorganisms

B16. Evaluate contaminant bioavailability and its relation to trophic/non-trophic transfer. Current understanding and models emphasize the trophic transfer of contaminants within the food chain. In light of advection, diffusion, and ebullition processes, non-trophic contaminant transfer requires better quantification to determine its importance and site-specific attributes. Specific projects and questions relevant to this data gap include:

- Determine the extent to which porewater concentrations are an accurate reflection of contaminant bioavailability
- Improve ability to sample/measure small volumes of porewater for organics
- Quantify trophic (particulate) and non-trophic (non-particle bound) transfer and bioaccumulation of contaminants across the food chain

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

46

- Develop reliable tools to monitor mechanisms/processes impacting contaminant flux

B17.   Assess synergistic technology opportunities in addition to individual technology improvements. Considering the scale and often challenging physical settings of contaminated sediments, it has become increasingly clear that in situ technologies should be considered synergistic rather than competitive.   Even if some combinations of site specificity and technology characteristics make more sense than others, significant strides in technology development may be gained from addressing treatment trains and otherwise combined approaches.   For example, combined bioremediation and phytoremediation, amendments of biotic and abiotic processes control, and combined capping and in situ technologies offer great potential for better engineered site management.

4.2.3 Summary
The deployment and consideration of in situ remediation technologies require substantial up-front and post-implementation monitoring and are highly dependent on site-specific characteristics. Considering the early stage and level of maturity of these technologies, the data gaps recognize the future needs for systems-level approaches to their development, scaled demonstration, and evaluation of performance characteristics. This requirement implies that proper operational and scaling constraints relevant to deployment should be adhered to for quantification of site- and technology-specific parameter uncertainties on the performance endpoints and economics. This issue is particularly pertinent considering the Superfund criteria for long-term effectiveness and permanence of any technology to protect human and ecosystem health and the current preference for dredging in remedial decision-making.

4.3 Monitored Natural Recovery

4.3.1 State of the Science and Engineering

4.3.1.1 Introduction and Background

Monitored natural recovery of sediments is a remedial strategy that consists of leaving contaminated sediments in place and allowing ongoing aquatic, sedimentary, and biological processes to contain, destroy, or otherwise reduce the bioavailability of the contaminants to protect receptors; it must be the result of a deliberate, thoughtful decision-making process following careful site assessment and characterization (NRC, 1997). MNR differs from "no action" alternatives in that source control, assessment, modeling, and monitoring efforts are required to verify that remediation (i.e., environmental processes to permanently reduce risk) is taking place. The primary benefits of MNR include avoidance of upland disposal requirements, minimal disturbance of sensitive habitats, and more cost-effective management of risks.

MNR for sediments is analogous to monitored natural attenuation (MNA) for soil and groundwater. The concept of MNA has been well documented for soils and groundwater, but guidance for applying MNR to sediments does not exist. The U.S. EPA document that comes closest to providing MNR guidance is the final U.S. EPA Office of Solid Waste and Emergency Response (OSWER) Directive, *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Sites* (OSWER Directive Number 9200.4-17P). This document, however, does not deal directly with sediments; rather, it contains a footnote that many of the same principles would be applicable to remediation of contaminated sediments. In December 2002, EPA produced a draft document titled *Contaminated Sediment Remediation Guidance at Hazardous Waste Sites* (U.S. EPA, 2002b). That document states that there is no presumptive remedy for contaminated sediments and that MNR should be evaluated at every site along with other active remedial options.

The evaluation of MNR relies on multiple lines of evidence to demonstrate sediment deposition and contaminant burial, attenuation, and transformation of sediment-bound contaminants, and perhaps most importantly, long-term ecological recovery and risk reduction. The following lines of evidence are used to support MNR (adapted from U.S. EPA, 2002b):

- Documentation (and possibly confirmation) of source control
- Evidence of contaminant burial and reduction of surface sediment concentrations
- Measurement of surface sediment mixing to estimate the active surface sediment benthic layer, and to determine the surface sediment depth to which remedial action objectives should be applied
- Measurement of sediment stability to assess the risk of contaminant resuspension under normal and high-energy events
- Evidence of contaminant transformation and risk attenuation
- Modeling of long-term recovery, including surface water, sediment, and biota
- Monitoring ecological recovery and long-term risk reduction

*SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments*

48

- Knowledge of future plans for use and development of the site and watershed, and institutional controls

All of the scientific tools and methodologies to generate these lines of evidence have not been fully developed at this time nor has their application to contaminated sediments as part of an MNR strategy been adequately demonstrated.

4.3.1.2 Monitored Natural Recovery: Maturity

4.3.1.2.1 Pilot-Scale/Full-Scale Demonstrations

More than 60 contaminated sediment projects have been remediated across the United States, but only two of them have implemented MNR as the primary remedial alternative (Thompson et al., 2003). Several projects have included MNR in combination with active remedies such as capping and/or dredging. At these sites, EPA acknowledged that attenuation (breakdown or dilution) was not necessary to demonstrate risk reduction in sediments and that physical processes (e.g., burial) play an important role in recovery. As a result, complete active remediation was not necessary at these sites (Thompson et al., 2003). The EPA acknowledged that partial dredging and/or capping, coupled with MNR for residuals, is a viable and practicable alternative for sediment management.

It is likely that smaller scale, site-specific demonstration tests of MNR of sediments are occurring at sites throughout the United States. However, the evaluation protocols being used and the robustness of the subsequent data sets are not being well documented, if at all.

4.3.1.2.2 Understanding of Underlying Principles

It is generally understood that impacted sediments will undergo some degree of physical and chemical recovery over time in many natural environmental settings. Most, if not all, of the MNR demonstrations to date document the continual deposition of sediments and progressive isolation of the impacts from the biota (i.e., physical recovery) as well as changes in bulk chemistry (primarily organic contaminants) and toxicity as evidence that MNR is occurring. Some of the underlying principles, e.g., chemical and/or biological reactions, that are responsible for these changes are not fully understood and have been, or are being, investigated in the laboratory and in small, field-scale experiments. However, due to the complexity of the natural environment and the extensive interactions that are taking place between the physical, chemical, and biological processes, the integrated picture of how MNR occurs is not well understood. For this reason, it is difficult to predict the performance of MNR at a given site and/or to consider enhancements to MNR that might be required to achieve the desired end state or the rate at which this end state is achieved. Similarly, when the desired end state is achieved, it is not possible to predict the permanence of the solution at a given site.

4.3.1.2.3 Barriers to Technology Use

The primary barriers to using MNR are: (1) lack of scientifically defensible, field-scale demonstrations dealing with a specific range/class of contaminants that confirm the ability of MNR to remediate impacted sediments to acceptable risk levels and (2) lack of a complete understanding of the underlying principles that govern the observed results. The lack of field demonstrations is the result of the long time periods that are required to determine the success of MNR combined with the relatively recent identification of MNR as a potential remedial strategy

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

49

for sediments. However, these demonstrations are necessary to convince the regulatory community and the public-at-large that MNR is capable of restoring the ecological functions of a sediment system. The lack of a complete understanding of the underlying principles is simply a reflection of the number of chemical, physical, and biological processes that are involved and the difficulty associated with mimicking a real, interactive sediment environment under laboratory conditions. However, an understanding at this level is necessary to predict the performance of MNR and to ensure that perturbations, e.g., changes in redox potential or pH, in the sediment system can be properly managed when they occur.

4.3.2 Primary Data Gaps in Monitored Natural Recovery

The primary research needs for MNR were identified in four general areas: (1) rapid screening assessment of the applicability of MNR to specific site; (2) long-term monitoring; (3) investigation of underlying principles; and (4) life cycle cost and risk analyses. Below, a short discussion of these general issues is followed by a listing of the high and moderate/low priority research needs for MNR of contaminated sediments. A more detailed description of the high and moderate/low priority research needs is provided after this listing.

Rapid Screening Assessment of the Applicability of MNR to Specific Sites

By its very nature, MNR requires relatively long periods of time, i.e., years, to complete treatment of impacted sediments. However, currently there are no validated techniques for rapidly assessing (i.e., periods of weeks to months) the applicability of MNR to a specific site (i.e., predicting its ability to achieve the desired end state as well as the time that is required for it to do so). This assessment is critical to making the decision to invest the time and money necessary to use MNR as the sediment remedial strategy.

Since the primary mechanisms of sediment treatment via MNR are sediment burial (i.e., elimination of the exposure pathway) and contaminant transformation (i.e., reduction of the toxicity of the impacted sediment), the ability to screen a site based on the potential for these two mechanisms to take place represent a high priority. With regard to the latter, it is also important to be able to define the treatment endpoint or the contaminant concentration in the sediment that will not yield an unacceptable impact to human health and the environment.

Long-Term Monitoring (Performance Assessment)

Given that MNR is a monitoring-intensive remedial strategy, there is a need for cost-effective long-term monitoring protocols, which would benefit greatly from the development and regulatory acceptance of in situ characterization/measurement techniques. The long-term monitoring of MNR should be designed to generate data that can be used to: (1) document the performance of MNR relative to the stated remedial objectives, (2) understand the inherent variability and uncertainties associated with the management of sediments using MNR, and (3) demonstrate that the primary biological, physical, and chemical processes that govern MNR are active and provide a basis for predicting their performance over time.

Not all of the characterization tools that are required for long-term monitoring currently exist, and those that do may require further development and/or refinement. Furthermore, due to the fact that MNR is a "characterization-intensive" remedial strategy and has the potential to require several years of monitoring, research is needed to define better, faster, and cheaper

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

50

characterization tools. To this end, there is an overriding preference to develop in situ characterization/measurement techniques as part of a long-term monitoring protocol.

Investigation of Underlying Principles

A better understanding of the underlying physical, chemical, and biological processes responsible for MNR is required to ensure that MNR performance can be accurately predicted and to ensure that the long-term monitoring programs are gathering the appropriate data for the evaluation of its performance. To examine these processes, it is recommended that a set of reference "study" sites be selected to provide a basis for systematic and multi-disciplinary field investigations. These reference sites provide a common field setting as well as a common source of sediment research samples for detailed laboratory investigations, should they be necessary to elucidate the fundamental physical and/or chemical mechanisms that are responsible for the field observations. To ensure that a consistent set of data are produced, all research samples should be centrally processed, characterized, and distributed to independent researchers investigating the various processes of interest. In addition, larger scale systems, such as mesocosms, should be considered as the platform to conduct this fundamental research. The use of a common suite of sediment research samples and larger scale mesocosms in combination with the field observations at a "reference" site will improve the ability of the sediment research to examine the integration of the various processes that are working behind the scenes during MNR.

The many different processes that contribute to MNR make it impossible to fully examine all of them at the laboratory scale. Consequently, there is a need to develop a preliminary process-based model of MNR that can be used to guide the detailed examination of the physical, chemical, and biological processes. The process-based model can be used to conduct sensitivity (i.e., what-if) analyses to isolate those parameters that are most important to understanding MNR. These high priority parameters can then be investigated and quantified at the laboratory or mesocosm scale.

Life-Cycle Cost and Risk Analyses

The temporal component of MNR requires the development and use of life-cycle cost and risk analyses to properly reflect the "lifetime" costs and risks associated with implementing this remedial strategy. The former is necessary to properly capture the cost of the long-term monitoring requirements while the latter is necessary to integrate the short-term risks associated with a site, which could conceivably increase over short periods of time, over the lifetime of the natural recovery process.

High Priority Research Needs

A26. Develop, evaluate, and/or validate a characterization tool to assess the stability of impacted sediments.

A27. Develop, evaluate, and /or validate a methodology to determine the desired end state that will yield environmentally acceptable sediment.

A28. Develop, evaluate, and/or validate characterization tools to determine the fraction of the sediment-bound contaminants that will be "treated" or "transformed" during MNR.

A29. Develop a Manual of Practice (MoP) for rapid screening and implementation of MNR at impacted sites.

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

51

A30.   Standardize approach on application, interpretation, and use of sediment flume data to assess sediment stability.

A31.   Develop tools to measure contaminant availability to pore water and ecological and human receptors (i.e., bioavailability).

A32.   Improve and/or develop ecological screening assays to predict ecological toxicity based on sediment chemistry in assessing the natural recovery of the impacted sediment over time during MNR.

A33.   Identify metabolites for contaminants of concern.

A34.   Determine the rates of attenuation of sediment-bound contaminants via microbiological action and/or abiotic reactions, including measurements of reaction byproducts.

A35.   Quantify the contaminant flux of sediment-bound contaminants into pore water and into organisms and examine the impacts of weathering and the presence of anthropogenic carbon on these flux profiles.

A36.   Develop relationships between sediment chemistry, sediment organic carbon content, contaminant flux from sediments, and organism uptake and toxicity.

A37.   Develop relationships between passive samplers and the results of both acute and chronic ecological assays.

A38.   Evaluate the life-cycle costs of MNR and develop a cost for implementation of the strategy that reflects the uncertainties of the input variables, i.e., probabilistic cost model.

Moderate/Low Priority Research Needs

B18.   Develop in situ techniques to rapidly determine the nature and diversity of the microbial consortia that exist in sediment.

B19.   Develop an in situ method for measuring redox potential.

B20.   Examine the effects of bioturbation on the "fabric" of the sediment and its subsequent impact on contaminant mobility.

B21.   Develop improved techniques for deciphering toxicity in sediments impacted by multiple contaminants (e.g., toxicity identification evaluations).

B22.   Develop a life-cycle risk evaluation protocol for MNR.

4.3.2.1 High Priority Research Needs

A26.   Develop, evaluate, and/or validate a characterization tool to assess the stability of impacted sediments.   An assessment of the stability of impacted sediments is required to determine if the sediment will be adequately contained during the time period that is required for MNR to achieve the desired ecological/biological end state. Such information is also critical to the design of an appropriate sampling plan to document the progress of MNR over time. Lastly, a rapid assessment of sediment deposition rates is also important since natural sediment burial represents one of the primary recovery processes of MNR. A standardized approach is needed to assess sediment stability that uses standardized measurement protocols and techniques to generate a consistent set of data that can be easily and accurately interpreted.

A27.   Develop, evaluate, and/or validate a methodology to determine the desired end state that will yield environmentally acceptable sediment.   It is important that the desired end state for the

impacted sediment be explicitly defined to serve as the benchmark for the evaluation of MNR and other sediment remediation strategies. For example, how much deposition is sufficient to ensure that exposure to impacted sediment has been adequately reduced and/or what contaminant concentrations must be achieved to eliminate the toxicity of the impacted sediment to the receptors of concern? Universally accepted methods to define these environmentally acceptable endpoints a priori are not currently available and must be developed for the proper evaluation and selection of a remedial strategy. For example, better techniques are required to estimate the toxicity of impacted sediment based on the sediment chemistry. One such technique is to use the bioavailable concentration of the bound contaminants rather than the total concentration as determined by conventional analytical techniques. Techniques to quantify the bioavailable fraction of sediment-bound contaminants should be developed and their use to estimate sediment toxicity and environmentally acceptable end states for sediments for a variety of test organisms should be validated.

A28. Develop, evaluate, and/or validate characterization tools to determine the fraction of the sediment-bound contaminants that will be "treated" or "transformed" during MNR. It is important to be able to rapidly assess the potential for MNR to achieve the desired end state, be it burial of the impacted sediment or a reduction in toxicity, or both. This ability would reduce the likelihood that MNR is selected for use at a site where it will not work, which may take years as well as substantial funds to evaluate. Based on the mechanisms that are likely to be dominant as part of MNR, it is hypothesized that it will "treat" or "remove" the bioavailable fraction of the bound-contaminant. As such, tools must be available to measure the bioavailable fraction of sediment-bound contaminants to provide a first order estimate of the extent of contaminants that will be removed during the course of MNR. Since it is hypothesized that toxicity is the result of the bioavailable fraction, MNR should also eliminate the toxicity at the same time that it is removing the bioavailable fraction.

A29. Develop a Manual of Practice (MoP) for rapid screening and implementation of MNR at impacted sites. It is important that the rapid site screening tools be validated as part of well designed field trials. To ensure that the proper data are collected in a consistent and technically defensible manner, an MoP or guidance document should be developed for RPMs that summarizes the state-of-the-art protocols that are available to evaluate and implement MNR at a DoD site. The data sets that are generated should be compiled and integrated into an MNR compendium that documents the adequacy of the rapid site assessment and long-term monitoring protocols and modifies them, as necessary, based on the field experience.

A30. Standardize approach on application, interpretation, and use of sediment flume data to assess sediment stability. To effectively conduct long-term monitoring of MNR, it is imperative that the movement of the impacted sediments throughout the site is understood. The methods and instruments that are needed for the completion of a sediment mass balance within a study area, i.e., optical sensors, acoustic techniques, and drawn-water sampling, are available. However, most sediment systems display significant temporal variability, which requires measurements to extend over long periods of time, often approaching 12 months or more. For this reason, very few projects have adequately addressed many of these issues; rather, models have been relied on for this purpose. While the development of models can also be expensive,

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

53

they are more easily obtained. Since there is not a lot of confidence in these models, more emphasis has to be placed on the design and systematic conduct of long-term field investigations.

A31. Develop tools to measure contaminant availability to pore water and ecological and human receptors (i.e., bioavailability).[7] Techniques are available for the in situ measurement of contaminant concentrations in pore water. These measurements are important since it has been established that contaminant concentrations in pore water correlate well with contaminant uptake by aquatic organisms as well as toxicity to these organisms. However, the current in situ techniques have not yet been perfected and require further development and field validation. Direct measurements of contaminant uptake by aquatic organisms can also be done but they are done ex situ, thereby requiring more time and expense.

A32. Improve and/or develop ecological screening assays to predict ecological toxicity based on sediment chemistry in assessing the natural recovery of the impacted sediment over time during MNR.[8] It is important to monitor the ecological recovery of a site throughout the duration of MNR to document that MNR is occurring and the rate at which it is occurring. State-of-the-art methods for conducting this monitoring include bioassay tests, which are lengthy and costly, and often yield results that are difficult to interpret. Improved methods to assess ecological recovery are required to reduce the cost and improve the uncertainty of the ecological monitoring protocols. Candidate methods include passive samplers (semi-permeable membrane devices) or genetic or endocrine indicators, and/or the use of sediment chemical analyses to predict ecological toxicity based on equilibrium partitioning models between sediment and pore water or sediment and ecological receptors. Standardization of biological sampling and analysis, the use of short-term biological deployments, e.g., caged fish, and assessments of the response of ecological food webs to improved sediment and pore water quality should also be investigated.

A33. Identify metabolites for contaminants of concern. The products that result from the transformation of the bioavailable contaminants during MNR must be tracked and/or understood to ensure that any secondary toxic effects are properly managed. This assessment is directly linked to ecological recovery. Specifically, it is important to assess the potential for reaction by-products to be released to the pore water and to determine its flux into the environment and uptake by aquatic organisms.

A34. Determine the rates of attenuation of sediment-bound contaminants via microbiological action and/or abiotic reactions, including measurements of reaction byproducts. The rates of attenuation of sediment-bound contaminants via microbiological action and/or abiotic reactions must be determined to provide the ability to estimate the effectiveness of MNR as a remedial strategy and to predict the time frame that will be required for MNR to achieve the desired end

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[7] This research need is strongly related to the high priority research needs under Section 3.1 (Fate and Transport of Contaminants) titled "A1. Develop and validate tools and techniques to assess site-specific bioavailability" and under Section 3.3 (Characterization of Contaminated Sediments) titled "A8: Develop, evaluate, and validate tools to determine the bioavailability and bioaccumulation of contaminants".

[8] This research need is strongly related to the high priority research need under Section 3.1 (Fate and Transport of Contaminants) titled "A3. Determine ecosystem shift and species disappearance as a result of the sediment contamination" and under Section 3.3 (Characterization of Contaminated Sediments) titled "A7: Develop, evaluate, and validate tools to efficiently monitor, assess the ecological risk, and assess the ecological recovery at contaminated sites".

state. Tests should be conducted to document the reactions that are occurring, the rate at which they occur, and the expected reaction byproducts, e.g., key metabolites.

A35. *Quantify the contaminant flux of sediment-bound contaminants into pore water and into organisms and examine the impacts of weathering and the presence of anthropogenic carbon on these flux profiles.* The flux of sediment-bound contaminants into pore water and the uptake of sediment-bound contaminants by aquatic organisms are strongly correlated to toxicity. These fluxes are more important than total contaminant concentration because of differences in bioavailability that are known to exist among sediments. Tests should be conducted to quantify the contaminant flux of sediment-bound contaminants into pore water and into organisms such as mussels or clams, and the impacts of weathering and the presence of anthropogenic carbon on these flux profiles should be assessed.

A36. *Develop relationships between sediment chemistry, sediment organic carbon content, contaminant flux from sediments and organism uptake and toxicity.* The equilibrium portioning model can be used to develop relationships between sediment chemistry and contaminant flux from sediments and organism uptake and toxicity. The state-of-the-art methods for using this model should be improved by (1) utilizing the bioavailable fraction of the sediment-bound contaminants and not their total concentration and (2) taking into account the amount and type of anthropogenic carbon that is present in the sediment. It has been shown that the ability to predict uptake and toxicity using the equilibrium partitioning model is vastly improved if these two modifications to the model are used, i.e., the uncertainty associated with predicting toxicity from sediment chemistry using the sediment equilibrium partitioning model can be significantly reduced. With this improved model, the chemical analysis of contaminants in sediment can be used, in lieu of biological assays, to track improvements in toxicity as a result of MNR processes.

A37. *Develop relationships between passive samplers and the results of both acute and chronic ecological assays.* Laboratory tests are needed to investigate the ability to use passive samplers, such as SPMDs, as surrogates for aquatic organisms for the purposes of estimating contaminant uptake and eventually predicting both acute and chronic ecological assays. The use of these chemical techniques has the potential to improve the accuracy and reduce the costs of using biological assays for this purpose at a field site.

A38. *Evaluate the life-cycle costs of MNR and develop a cost for implementation of the strategy that reflects the uncertainties of the input variables (i.e., probabilistic cost model).* A life-cycle cost analysis protocol should be developed for MNR based on the best information that is available to date. At the same time, a probabilistic cost model should be developed that can generate a statistical distribution of the cost of MNR based on the inherent uncertainties associated with its implementation, e.g., the rate of contaminant transformation or the extent and duration of the long-term monitoring program that is required. (Note: Probabilistic cost models can accept input variables expressed as a statistical distribution rather than a point value.) In this manner, the uncertainty of an input variable can be quantitatively captured and reflected in a statistical distribution for the cost output of the model. As the MNR research is conducted, the inputs to the life-cycle and probability cost analyses can be revised as they become better understood and their uncertainty is reduced, further refining the cost output of the models. These

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

55

cost models, along with the process-based model, can also be used to identify which elements of an MNR strategy make the greatest contribution to the life-cycle cost and warrant further investigation.

4.3.2.2 Moderate/Low Priority Research Needs

B18. Develop in situ techniques to rapidly determine the nature and diversity of the microbial consortia that exist in sediment. Since biological action is believed to be one of the primary mechanisms of contaminant transformation during MNR of sediments, there is a need for in situ techniques that can rapidly determine the nature and diversity of the microbial consortia that exist in sediment. The determination of the presence of these consortia prior to sediment management will indicate the feasibility of using MNR as a remedial strategy. Similar assessments over time will indicate if MNR is occurring and whether or not the consortia is changing over time, which can affect the rate at which MNR occurs. The monitoring of the metabolites that are formed during biological transformation should be done in tandem with these biological measurements. To effectively monitor these chemicals, hypotheses regarding the contaminant transformation pathways are also needed.

B19. Develop an in situ method for measuring redox potential. There is evidence that the oxidation-reduction potential can affect the bioavailability of sediment-bound organic contaminants as well as the bioavailability and chemical form of certain metal contaminants. For this reason, reliable field methods, ideally in situ field methods, are needed to measure redox potential during MNR of sediments. Characterization tools or screening assays for other chemical or geochemical parameters may also be needed. However, the identification of these parameters and their relative importance to the MNR strategy will have to be evaluated based on laboratory screening studies followed by the use of a process-based MNR model to assess the importance of the individual parameters on the overall effectiveness of MNR as a sediment remedial strategy.

B20. Examine the effects of bioturbation on the "fabric" of the sediment and its subsequent impact on contaminant mobility. The activity of biota in the sediment can result in changes to the sediment structure or fabric over time (e.g., porosity). These changes, otherwise known as bioturbations, have the potential to alter the mobility of the sediment-bound contaminants and ultimately, the exposure of ecological receptors to these contaminants. Studies are needed to investigate the extent and nature of bioturbation and to document its effect on contaminant mobility. Methods and techniques to measure these effects in the field should be developed to permit the field validation of these effects following their documentation at the laboratory scale.

B21. Develop improved techniques for deciphering toxicity in sediments impacted by multiple contaminants (e.g., toxicity identification evaluations). There is a need for more rapid and cost-effective methods to assess the cause and effect relationships between the sediment-bound contaminants and the resulting acute or chronic toxicity. The current methods (i.e., toxicity identification evaluations [TIE]) are cumbersome and expensive. They involve a series of tests where the sediment chemistry is modified in a stepwise fashion and toxicity evaluations are systematically repeated following each modification. An examination of these toxicity responses to the known changes in sediment chemistry yields information as to the specific causes of the

SERDP & ESTCP Expert Panel Workshop on Research & Development Needs for the In Situ Management of Contaminated Sediments

56

toxicity. Improvements to this current approach would greatly improve the ability to target, and potentially reduce the costs of, sediment remediation strategies.

B22. Develop a life-cycle risk evaluation protocol for MNR. This need is driven by the long time frame associated with this remedial strategy and the fact that the chemical, biological, and physical changes that occur during MNR may result in temporal changes (both increases and decreases) in the short-term risk associated with a site. To address this potential for temporal fluctuations in the risk profile for a site and to put them into proper perspective, the risk assessment protocol must be able to incorporate the point estimates of risk over the lifetime of the MNR and integrate them into an overall risk evaluation of this sediment remedial strategy.

4.3.3 Summary
There are three overarching, high priority research needs that should be addressed to establish a framework for systematically examining MNR of sediments. The first of these is a need for an MNR MoP or guidance document. The purpose of this document is to provide remedial project managers with the protocols for implementing MNR and documenting its performance. This document should draw upon the current state-of-the-art methods and techniques to provide specific direction for assessing and validating MNR at a sediment site. Second, there is a need to apply the elements of the MoP at a range of DoD sediment sites that represent a full spectrum of contaminant characteristics and concentrations as well as different sedimentary environments. From these case studies, the MoP will be refined, as necessary, and any limitations in applying MNR to specific sites will be documented. For example, MNR may not be applicable at high-energy sites simply because the physical instability of the sediment precludes implementing a successful, long-term monitoring program. If properly selected, the case studies will define the range of site conditions that are amenable to MNR as a sediment remediation strategy. Lastly, there is a need for a preliminary process-based model of MNR that can be used to make initial predictions of the expected performance as well as guide the detailed examination of the physical, chemical, and biological processes. As previously noted, there are many different processes that contribute to MNR, making it impossible to fully examine all of them at the laboratory scale. A basic process model can be used to conduct sensitivity analyses that will isolate those parameters that are most important to understanding MNR. These parameters can then be investigated and quantified at the laboratory or mesocosm scale. Lastly, overarching technology evaluation protocols should be developed to assess the cost (i.e., probabilistic cost model and life-cycle cost analysis) and life-cycle risks associated with sediment MNR.

With these assessment/evaluation frameworks in place, the development of MNR as a viable sediment management strategy will require the systematic conduct of parallel research efforts in the field and in the laboratory (bench-scale or mesocosms). A systematic approach is necessary to ensure that each element of the research is built on what is learned from the previous research efforts. The emphasis on field efforts will provide the evidence that MNR does indeed occur and that it is able to achieve the desired sediment end state in a reasonable amount of time. A significant part of the field studies will be to develop and demonstrate rapid screening of candidate sites and long-term monitoring MNR protocols for the basic physical, chemical, and biological processes that are critical to MNR. The companion laboratory studies, if required, will emphasize a more fundamental examination of these same processes, including contaminant attenuation, contaminant bioavailability, contaminant partitioning into pore water and aquatic organisms, and sediment stability.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

57

5. CONCLUDING THOUGHTS

Aquatic sediments are often the ultimate receptors of contaminants in effluent from DoD activities. Sediment contamination problems are particularly difficult due to the tendency for contaminants to be retained within sediments for a long time. Further complexities include the multiplicity of contaminants often found at such sites, the different matrices in which these contaminants are found, the numerous physical compartments typical of such systems, and the highly complex processes governing contaminant exchange between system compartments and subsequent transport and fate. Based on more than 200 identified sites, the estimated cost to complete remediation of the Navy's contaminated aquatic sediments is more than $1 billion. As estuarine and coastal sites fall under increasing scrutiny, the number of DoD sites requiring action is likely to increase.

There is a need for sound science and effective tools to characterize and manage these DoD sites in a manner that reduces risk to human health and the environment and gains regulatory acceptance. Despite years of investigation by many researchers in the field, it is clear that much remains unknown and that an integrated approach to addressing these gaps is required. SERDP and ESTCP, as DoD programs that promote the development and demonstration of innovative, cost-effective environmental technologies, must determine how their limited funds can best be invested to improve DoD's ability to effectively address its cleanup requirements. Advancing the science and engineering of in-place management approaches for contaminated sediments has significant potential to impact future cleanup actions by DoD and was the focus of this workshop

Throughout the workshop, the interrelationship of physical, chemical, and biological processes affecting contaminant fate, transport, and exposure became apparent as did the importance of understanding these processes when selecting, implementing, and assessing the performance of an in situ management approach. In particular, the ability to evaluate sediment stability and the fate and transport of contaminants is inextricably linked with site characterization efforts. In turn, these characterization efforts determine the type of management approach (capping, in situ treatment, or MNR) that is appropriate for a particular site. The ultimate goal is to define a set of environmental conditions for which technologies are appropriate, such that their transferability between field sites is facilitated. In addition, guidance will be required to aid RPMs in making cost-effective and environmentally sound decisions about in situ management approaches for contaminated sediments. Regulatory acceptance for in situ management approaches (as opposed to dredging) is dependent on continued investigation.

The result of this workshop is a strategic plan to guide investments in the area of contaminated sediments by SERDP and ESTCP over the next 5 years. In addition to the research needs prioritized and described throughout this report, overarching recommendations in terms of areas to focus future efforts follow.

6. RECOMMENDATIONS

In order to better integrate research, development, test, and evaluation efforts supported by SERDP and ESTCP, workshop participants highlighted several overarching recommendations to guide future investments over the next 5 years. These recommendations reflect high-priority DoD needs in the area of contaminated sediments. While some recommendations are technology-specific, others encompass numerous processes and technologies. Recommendations range from fundamental to applied.

6.1 Investigative Tools

Due to the complexity of the natural environment and the extensive interactions that are taking place between the physical, chemical, and biological processes at contaminated sediment sites, investigative tools are required to identify and predict the rates of the most important processes affecting contaminant fate, transport, and exposure at a particular site or sites in general. Knowledge of these processes and their rates is critical to the development and refinement of site conceptual models, which impact the selection and implementation of a management approach in the field. Further, there is a need to consider what one measures to evaluate technology effectiveness. Performance assessment is particularly relevant for in situ management approaches (e.g., capping and MNR) where long-term monitoring requirements are high. Workshop participants called for the development of rapid, inexpensive, and standardized tools to measure the rates of key sediment chemistry, physics, and biological processes (e.g., redox, dissolved oxygen, seepage, contaminant flux, critical shear stress, erosion, bioavailability, etc.).

6.2 Analysis Tools

Many analysis tools are available for organizing, interpreting, and extrapolating the various types of characterization data obtained at contaminated sediment sites; however, improvements are required to determine the relationships and interactions among the processes, model the interactions of processes, and forecast the success of different remedial alternatives. Also, it is important to facilitate the selection, development, and validation of process-based models constrained by accurate measurements of key chemical, physical, and biological processes. Standardized methods are needed to incorporate uncertainty in time and space into all levels of site characterization and into all tiers of predictive fate and transport models (based on a CSM).

6.3 Effectiveness of Capping

Within the area of capping, workshop participants urged fundamental studies to investigate the effectiveness of both active and passive caps. Issues surrounding the effectiveness of caps included placement, thickness, gas ebullition, kinetics of recolonization, bioavailability of sequestered contaminants, and erosion resistance. Further, it was noted that performance metrics are required to assess effectiveness.

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

59

6.4 MNR Guidance

Currently, it is difficult to predict the performance of MNR at a given site and/or to consider enhancements to MNR that might be required to achieve the desired end state or the rate at which this end state is achieved. Similarly, when the desired end state is achieved, it is not possible to predict the permanence of the solution at a given site. Development of an MoP or guidance document would provide RPMs with the protocols for implementing MNR and documenting its performance. This document should draw on the current state-of-the-art methods and techniques to provide specific direction for assessing and validating MNR at a field site. Once developed, the elements of the MoP should be applied at a range of DoD sites that represent a full spectrum of contaminant characteristics and concentrations as well as different sedimentary environments to define the range of site conditions that are amenable to MNR as a contaminated sediment remediation strategy.

6.5 Delivery of In Situ Amendments

To realize the potential of in situ sediment remediation for overall protectiveness and permanence, while satisfying the regulatory preference for reduction of toxicity, mobility, or volume through treatment, the issues associated with effective amendment delivery to cohesive sediment matrices must be overcome. Workshop participants recommended that fixed and mobile technologies be developed and demonstrated for delivery of aqueous, particulate, and gaseous amendments to treat sediments with minimal sediment resuspension and disturbance of benthic ecologies. Considering the early stage and level of maturity of these technologies, systems-level approaches to their development, scaled demonstration, and evaluation of performance characteristics should be undertaken.

6.6 Standardized Test Sites

Workshop participants recommended that as many as three standardized test sites be established where in-place management approaches to contaminated sediments can be effectively evaluated and compared to one another under a defined set of conditions. Generally, the site specificity of sediment matrices, physical forcings, and contaminant history hampers effective technology transfer between sites. Deployment and demonstration of technologies at standardized test sites with widely differing characteristics also will facilitate the development of performance metrics (e.g., short- and long-term effects on sediment stability, contaminant flux, and ecological communities).

6.7 Data Mining

A common theme during breakout group discussions was the untapped wealth of information and data available from pilot- and full-scale demonstrations ongoing or completed at contaminated sediment sites. By investigating existing in situ management approaches to contaminated sediments, lessons learned can be identified with the ultimate goal of developing a decision tree for RPMs to use in selecting, designing, and implementing a remedial approach at their field site. In some cases, support for additional monitoring events following an in situ management approach may help to verify predictions of the types and rates of processes

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

60

impacting contamination and its treatment at field sites. Specific suggestions for such "data mining" included reviewing existing applications of capping technologies and MNR (see Sections 4.1 and 4.3).

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62

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63

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64

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*SERDP & ESTCP Expert Panel Workshop on Research &
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SERDP & ESTCP Expert Panel Workshop on Research &
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A-7

APPENDIX B

AGENDA

CONTAMINATED SEDIMENTS WORKSHOP

Omni Hotel - Charlottesville, Virginia

TUESDAY, AUGUST 10, 2004		
0800	Continental Breakfast and Registration	

0830	**Welcome and Introduction**	Mr. Brad Smith
		  SERDP Executive Director
		Dr. Jeff Marqusee
		  ESTCP Director
		Dr. Andrea Leeson
		  SERDP/ESTCP Cleanup
		  Program Manager

0845	**Navy Overview:** Extent of Problem, Policy, & Technology Needs	Mr. Jason Speicher
		Mr. Michael Pound
		  Naval Facilities
		  Engineering Command

0910	**Army Overview:** Extent of Problem, Policy, & Technology Needs	Dr. Todd Bridges U.S. Army ERDC
Overview of Background Papers on State of Science and Engineering		
0930	Sediment Stability Issues	Dr. Tom Ravens Texas A&M at Galveston
0955	Fate and Transport of Contaminants	Dr. Rebecca Dickhut VIMS
1020	Characterization of Contaminated Sediments	Dr. Tim Dekker Limno-Tech, Inc.
1045	Break	
1100	**Breakout Session I Discussions: Key Processes** • Sediment Stability Issues (Madison Room) • Fate and Transport of Contaminants (Salon C) • Characterization of Contaminated Sediments (Montpelier Room)	Breakout Groups
1200	Working Lunch (Lunch Provided)	
1300	**Breakout Session I Discussions (cont'd)** • Sediment Stability Issues (Madison Room) • Fate and Transport of Contaminants (Salon C) • Characterization of Contaminated Sediments (Montpelier Room)	Breakout Groups
1500	Break	
1530	**Reports from Breakout Session I and Discussion (Salon C)**	Breakout Group Chairs
1700	**Adjourn**	

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

B-1

WEDNESDAY, AUGUST 11, 2004		
0800	Continental Breakfast	
	Overview of Background Papers on State of Science and Engineering	
0830	Capping	Dr. Danny Reible Louisiana State University
0855	In Situ Treatment	Dr. John Wolfe Limno-Tech, Inc.
0920	Monitored Natural Recovery	Dr. Victor Magar Battelle Memorial Institute
0945	Break	
1000	**Breakout Session II Discussions: In-Place Management** (3 Small Groups Addressing All Approaches) • Group 1 (Madison Room) • Group 2 (Salon C) • Group 3 (Montpelier Room)	Breakout Groups
1200	Working Lunch (Lunch Provided)	
1300	**Breakout Session II Discussions (cont'd)**	Breakout Groups
1500	Break	
1530	**Reports from Breakout Session II and Discussion (Salon C)**	Breakout Group Chairs

1700	**Closing Remarks**	Mr. Brad Smith
		  SERDP Executive Director
		Dr. Jeff Marqusee
		  ESTCP Director
		Dr. Andrea Leeson
		  SERDP/ESTCP Cleanup
		  Program Manager

1715	**Adjourn**	

THURSDAY, AUGUST 12, 2004	
0800	Continental Breakfast for Breakout Session Rapporteurs
0830	**Discuss and Prepare Draft Sections of Summary Document (Breakout Session Rapporteurs)**
1200	**Adjourn**

SERDP & ESTCP Expert Panel Workshop on Research &
Development Needs for the In Situ Management of Contaminated Sediments

B-2